



Civil Engineering
and Geosciences



Newcastle
University

**REMEDIATION OF HEAVY METAL CONTAMINATED FINE
GRAINED SOILS USING ELECTROKINETIC GEOSYNTHETICS**

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**A thesis submitted to the University of Newcastle upon Tyne in partial fulfilment of the
requirement for the degree of Doctor of Philosophy**

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DECLARATION

I, **Denis Kalumba**, hereby declare that this thesis is essentially my own work, except where otherwise specified, and has not nor the original work contained there in, to the best of my knowledge, been submitted for a degree at any other university or high institution of learning.

.....

Denis Kalumba,
31st August 2006

TO

My wife, PHUMZILE, daughters, SINDI & KETHI and son, ED.

Next to the Lord, JESUS CHRIST, you are my dearest.

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Mukama Yebazibwe.

Denis Kalumba

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SYNOPSIS

Among the most promising novel methods for treating heavy metal contamination in fine soils is electrokinetic soil remediation – passing a low-voltage current through the soil that causes the target contaminants to migrate to the electrodes, where they can be captured, broken down or immobilized. However, the widespread in-situ application of this process as a creative solution for the problem of metal contamination has been prevented because of a variety of problems, some of which are linked to the available electrodes. The limitations related to the available electrodes include: corrosion of the anodes, difficulties in removing contaminated water and gases from the electrodes, poor electrical contact of electrodes with the soil, cost of producing functioning electrodes, and limitations related to the physical form of the electrodes. Many of these historical limitations have been eliminated by the introduction of Electrokinetic Geosynthetics (EKGs) which combine electrokinetics with geosynthetics technology to create geosynthetic electrodes.

In this investigation, the use of an EKG system to capture and dispose of zinc ions from kaolin soil is evaluated by conducting extensive laboratory tests using specially designed bench scale tanks. A comprehensive test programme was established to include two electrokinetic remediation removal approaches: One Process Approach and Two Process Approach. The former was achieved by electro migration of metal contaminants towards the cathode electrode without any external enhancement agent while the latter combined soil flushing with the electrokinetic process. The testing technique enabled the study of effects of: water flushing, soil depth, intermittent currents and replenishing draining chambers along the soil profile with deionised water, on the efficiency of cation removal. The respective responses were primarily presented in terms of electrical current/test duration, water content/test duration, zinc concentration/normalised distance from the anode, zinc concentration/ test duration and pH/ normalised distance from the anode.

Results indicated that the EKG system has a lot of potential for cleaning up soil at sites contaminated by heavy metals and other harmful compounds. The in-depth analysis also showed clearly that combining the technique with soil flushing improved the effectiveness of the treatment operation. The study considerably extended the understanding of the performance of electrokinetic technology particularly in fine grained soil and areas where further research would improve this understanding were highlighted.

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LIST OF ABBREVIATIONS

A	-	Cross-Sectional Area
AAS	-	Atomic Absorption Spectrometer
Ar	-	Arsenic
As	-	Arsenic
BS	-	British Standards
Ca	-	Calcium
Cd	-	Cadmium
Co	-	Cobalt
Cr	-	Chromium
Cu	-	Copper
D	-	Diameter
DC	-	Direct Current
EDTA	-	Ethylenediamine Tetraacetic Acid
EK	-	Electrokinetic(s)
EKG	-	Electrokinetic Geosynthetic
EKGs	-	Electrokinetic Geosynthetics
Fe	-	Iron
g	-	Grams
H	-	Height
HCl	-	Hydrochloric Acid
Hg	-	Mercury
k_e	-	Electroosmotic Permeability
l	-	Litre(s)
L	-	Length
Lab	-	Laboratory
m	-	Metre(s)
WC	-	Water Content
WCs	-	Water Contents
Meq	-	Milliequivalent
Mg	-	Magnesium
mg	-	Milligram(s)
ml	-	Millilitre(s)

mm	-	Millimetre(s)
mol	-	Mole
Na	-	Sodium
Ni	-	Nickel
PAHs	-	Polycyclic Aromatic Hydrocarbons
Pb	-	Lead
PCBs	-	Polychlorinated Biphenyls
Q	-	Electroosmotic Fluid Volume Flow Rate
Sr	-	Strontium
T	-	Time
UK	-	United Kingdom
V	-	Voltage
VDC	-	Voltage Direct Current
VOCs	-	Volatile Organic Compounds
Vol	-	Volume
W	-	Width
Z	-	Depth
Zn	-	Zinc
μm	-	Micrometre(s)
ζ	-	Zeta Potential

INTRODUCTION

1.0 General

Growing pressure on land resources and greater environmental awareness has led to an increasing need to reclaim and recycle contaminated land. To date some 50% of all development in the United Kingdom is taking place on previously used land, some of which may be contaminated (Sarsby 2000). For instance, the U.K. is currently undergoing something of a housing crisis which has led to rising house prices – there is a large demand for housing, but land is relatively scarce upon which to build, especially non-green belt land. To attempt to minimise urban sprawl, the UK Government has indicated that by the year 2010, at least 60% of new housing should be constructed on brownfield sites – previously developed lands (Parliamentary Office of Science and Technology, 1998). A good source of brownfield sites is the wealth of former industrial land, often located in the centre of cities and large towns. However, there is a greater risk of this land being contaminated due to its previous uses, and so before construction can begin, the land may have to be remediated. By not remediating, the risk of exposing construction workers or the general public to a formerly ‘dormant’ chemical reservoir is greatly increased. And yet diseases of contamination are qualitatively different from infectious diseases or lifestyle diseases. They cannot be fought with vaccines, antibiotics or changes in lifestyle. The only solution is to get to the source of the toxicity and either remove it, make it safe or lock it up.

Therefore, before any development can take place, it is important to identify and characterize contaminated sites in terms of the nature and extent of contamination and consequential threat posed by such sites to human health and the environment. Unfortunately, once this has been done developers are reluctant to rehabilitate them because of the high cost associated to clean up.

Section 57 of the Environment Act 1995 defines contaminated land as: “Any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on, or under the land that:

1. Significant harm is being caused, or there is a significant possibility of such harm being caused; or
2. Pollution of controlled waters is being, or is likely to be, caused.”

Thus, a site is considered contaminated if:

- because of its former use, now contains substances that present hazards likely to affect its development, and/or
- requires an assessment to determine whether redevelopment should proceed without some form of remediation of the site.

1.1 Problem Statement

The legacy of the 18th century (and longer) industrial revolution and the wide spread ignorance of the effects of industrial activity have left behind a large stock of contaminated land in the UK. Thousands of sites have had potentially contaminating uses, and while many are known about, others remain to be discovered. The main causes of this contamination were; minerals from mining, leaks and spills at factories, disposal of wastes in uncontained landfill sites and the discharge of many chemicals associated with agrochemicals in farm fields. Figure 1.1 shows an example of such a site where mine water is being led into unprotected grounds contaminating the underlying soils and ground water.



Fig 1.1 Site Being Polluted with Heavy Metals from Industrial Effluent

By the beginning of the last decade, estimates of the scale varied between 50,000 and 100,000 potentially contaminated sites, covering between 50,000 and 100,000 hectares in England and Wales (ENDS 1991). The Environment Agency recently estimated that at least 300,000 hectares of land could be affected by contamination. This covers almost 1% of the land area of Great Britain. The Agency states that the number of sites requiring remediation is likely to be between 5,000 and 20,000.

On most contaminated sites, typical contamination takes the form of heavy metals and organics as well as substances specific to certain industries. However, as compared to toxic organics and inorganics, that in many cases can be degraded, the metallic species that are released into the environment tend to persist indefinitely, accumulating in living tissues throughout the food chain. Metal pollutants such as arsenic, cadmium, mercury, copper, chromium and zinc cannot be broken down to non-toxic forms.

The Confederation of British Industry (CBI) estimates that the cost of decontaminating land in the UK, using currently approved technologies, could reach a staggering £20 billion. These technologies focus on processes that include dig and dump, solidification and stabilisation, soil flushing, encapsulation, etc. Although in some instances successfully applied, the effectiveness and efficiency of these approaches as in the case of heavy metals removal has been questioned by practitioners. They are failing to reduce the legacy of contaminated land, making their approach environmentally unsustainable.

Furthermore, the local geology of almost all these affected sites consists of consolidated low permeable fine soils. Contamination in such low permeable soil poses a significant technical challenge for in-situ remediation efforts. Poor accessibility to contaminants and difficulty in delivering treatment reagents have rendered most existing in-situ treatments rather ineffective and the operations to clean such soils are often costly.

In this study the possibility of developing a technology, which could be applied specifically in cleaning up metal contamination in low permeability soils in situ, was investigated. Using electrokinetic geosynthetics (EKGs), which were electrically conductive geosynthetics as electrodes, the technology coupled electrokinetics for contaminant transport in the soil matrix with soil flushing method.

EKGs are electrically conductive geosynthetics whose new application has been created by incorporating electrokinetic phenomenon with the existing traditional functions of geosynthetic materials.

The proposed technology combined electrokinetics within the treatment zones that were formed by installing EKGs directly in the contaminated soils to form an integrated remedial process. The aim of the electrokinetics was to transport pollutants scattered all over the soil towards wells where they could be collected. This goal is effected by the migration of subsurface contaminants in an imposed electric field via electromigration and washed across by electroosmosis. While the purpose of soil flushing was to provide the necessary water required to transport the contaminants.

1.2 Significance of the Study

A truly robust and reliable in-situ remediation technology is desirable for the remediation industry, especially for heavy metal contaminants in low permeability soils such as clays, which are traditionally difficult to remediate with current methods. Because of the potential of electrokinetic process to treat a wide range of contaminants, it was hoped that the use of EKG to remediate soil would develop into a main line technology that will make the UK's contaminated sites clean-up programme much cheaper than is now predicted.

Of course, once fully developed, the technology would have tremendous benefits over existing ones in many aspects including environmental impacts, cost effectiveness, waste generation, treatment flexibility and breadth of other applications. It would definitely allow a more rapid and efficient remediation of fine-grained soils without the need to dig and dump. Success of the study, therefore, was expected to begin the process of producing an important in-situ means of environmental restoration. Further development is recommended in order to create a fully developed technique.

1.3 Thesis Overview

This chapter initially introduces the topic to be investigated and provides the reader with an appropriate background of the issue, its importance and problems already at hand.

Chapter 2 describes the literature associated with soil-remediating technologies, with respect to heavy metal remediation, pointing out their strengths and drawbacks. Emphasis

is placed on electrokinetic soil remediation technology in order to gain basic understanding of: (i) the electrokinetic technique as applied in soil remediation, and (ii) the fundamental mechanism of the technology. Specific literature review of previous research effort performed using the electrokinetic process, to remediate heavy metal contaminated soils, is also undertaken in order to establish a sound basis for achieving the objectives of this work. From the information gained in the literature, research objectives and philosophy were formulated and are presented in Chapter 3.

In Chapter 4, the methodology applied in order to undertake this investigation is presented. The design of the suitable bench-scale laboratory apparatus, as well as the concept of soil preparation and contamination protocols is presented. The research materials used are detailed and consequently discussed.

Data collected from the resulting laboratory programme are presented in Chapter 5 and discussed in detail in Chapter 6. The culminations of the discussion are the novel algorithms that resulted from the examination of the findings from the experiments. The application and merits of the developed EKG remediation concept is included at the end of the chapter.

Finally, Chapter 7 summarizes and underlines the most important conclusions derived in this fundamental research. Further efforts motivated by this work and its findings are recommended at the end of the chapter.

LITERATURE REVIEW

2.0 Introduction

In recent years, there has been increasing interest in finding new and innovative solutions for the efficient removal of contaminants from soils to solve soil, as well as groundwater, pollution problems. The objective of this review is to examine several alternative soil-remediating technologies, with respect to heavy metal remediation, pointing out their strengths and drawbacks and placing an emphasis on electrokinetic soil remediation technology. The discussion divides the treatment processes into ex-situ and in-situ methods.

In addition, the chapter presents detailed theoretical aspects of the electrokinetic transport mechanisms and the different physicochemical processes that occur during the electrokinetic remediation of soils. The design and operational considerations of electrokinetic soil-remediation variables, which are most important in efficient process application, as well as the advantages over other methods and obstacles to overcome, are also discussed.

Then, several emerging in-situ electrokinetic soil remediation technologies, such as LasagnaTM, Elektro-KleanTM, etc., are also looked at, and their advantages, disadvantages and possibilities in full-scale commercial applications are examined. An over view of these techniques, which in essence, provides a justification for the specifically selected techniques for this study, is presented.

The previous laboratory and field studies, using electrokinetic technology to extract heavy metals from contaminated soils, are presented.

Finally, the effort defines and discusses the concept of electrokinetic geosynthetic (EKG) highlighting the benefits of using these materials as electrodes in electrokinetic remediation.

2.1 Sources of Metal Contaminants

Metal-bearing solids and ground water at contaminated sites can originate from a wide variety of sources in the form of airborne emissions, process solid wastes, sludges or spills much of which result from manufacturing or other industrial activities/operations (Asante-Duah, 1996). Each of these contaminant sources influences the heterogeneity of contaminated sites on a macroscopic and microscopic scale. Variations in contaminant concentration and matrix influence the risks associated with metal contamination and thereby influence the cleaning options (Evanko and Dzombak, 1997). Table 2.1 shows the main industries and activities that give rise to contaminated land problems.

2.1.1 Airborne Sources

Airborne sources of metals include stack or duct emissions of air, gas, or vapour streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as arsenic, cadmium, and lead can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained (Smith et al., 1995).

Stack emissions can be distributed over a wide area by natural air currents until dry and/or wet precipitation mechanisms remove them from the gas stream. Fugitive emissions are often distributed over a much smaller area because emissions are made near the ground. In general, contaminant concentrations are lower in fugitive emissions compared to stack emissions. The type and concentration of metals emitted from both types of sources will depend on site-specific conditions (Evanko and Dzombak, 1997).

2.1.2 Process Solid Wastes

Process solid wastes can result from a variety of industrial processes. These metal-bearing solid wastes are disposed above ground in waste piles or below ground or under cover in landfills. Examples of process solid wastes include slags, fly ash, mold sands, abrasive wastes, ion exchange resins, spent catalysts, spent activated carbon, and refractory bricks (Zimmerman and Coles, 1992).

Table 2.1 Catalogue of Contaminant Source and their Typical Hazards (Adapted from Asante-Duah, 1996)

Source	Typical Hazards
Agricultural and Food Production	Acids and Alkalis; Fertilizers (e.g. nitrates); Herbicides (e.g., dioxins); Insecticides; Unused pesticides (e.g. DDT)
Airports	Hydraulic fluids; Oils
Auto/Vehicle Servicing	Acids and Alkalis; Heavy metals; lead-acid batteries (e.g. cadmium, lead, nickel); Solvents; Waste Oils
Chemical/Pharmaceutical Industry	Acids and Alkalis; Biocide wastes; Cyanide wastes; Heavy metals (e.g. arsenic mercury); Infectious and Laboratory wastes; Organic residues; PCBs; Solvents
Domestic	Acids and alkalis; Dry-cell batteries (e.g. cadmium, mercury, zinc); Heavy metals; Insecticides; Solvents (e.g. ethanol, kerosene)
Dry Cleaning / Laundries	Detergents (e.g. boron, phosphates); Dry cleaning filtration residues; Halogenated solvents
Educational / Research Institutions	Acids and Alkalis; Ignitable wastes; Reactives (e.g. chromic acid, cyanides; hypochlorites, organic peroxides, perchlorates, sulphides); Solvents
Electrical Transformers	Polychlorinated biphenyls (PCBs)
Equipment Repair	Acids and Alkalis; Ignitable wastes; Solvents
Leather Tanning	Inorganics (e.g. cadmium, lead); Solvents
Machinery Manufacturing	Acids and Alkalis; Cyanide wastes; Heavy metals (e.g. cadmium, lead); Oils; Solvents
Medical/Health Services	Laboratory wastes; Pathogenic/Infectious wastes; Radio nuclides; Solvents
Metal Treating / Manufacture	Acids and Alkalis; Cyanide wastes; Heavy metals (e.g. antimony, arsenic, cadmium, cobalt); Ignitable wastes; Reactives; Solvents (e.g. toluene, xylenes)
Military Training Grounds	Heavy metals
Mineral Processing / Extraction	High-volume/Low-hazard wastes (e.g. mine tailings); Red muds
Motor Freight/Railroad Terminals	Acids and Alkalis; Heavy metals; Ignitable wastes (e.g. acetone; benzene; methanol); Lead-acid batteries; Solvents
Paint Manufacture	Heavy metals (e.g. antimony, cadmium, chromium); PCBs; Solvents; Toxic pigments (e.g. chromium oxide)
Paper Manufacture/ Printing	Acids and Alkalis; Dyes; Heavy metals (e.g. chromium, lead); Inks; Paints and Resins; Solvents
Petrochemical Industry / Fueling Stations	Benzo-a-pyrene (BaP); Hydrocarbons; Oily wastes; Lead; Phenols; Spent catalysts
Photo finishing / Photographic Industry	Acids; Silver; Solvents
Plastic Materials and Synthetics	Heavy metals (e.g. antimony, cadmium, copper, mercury); Organic Solvents
Shipyards and Repair Shops	Heavy metals (e.g. arsenic, mercury tin); Solvents
Textile Processing	Dyestuff; Heavy metals and compounds (e.g. antimony, arsenic, cadmium, chromium, mercury, lead, nickel); Halogenated solvents; Mineral acids; PCBs
Timber/Wood Preserving Industry	Heavy metals (e.g. arsenic); Non-halogenated solvents; Oily wastes; Preserving agents (e.g. creosote, chromated copper arsenate, pentachlorophenol)

Because waste piles are above ground, they are exposed to weathering which can disperse the waste pile to the surrounding soil, water and air and can result in generation of leachate which infiltrates into the subsurface environment. The ability of landfills to contain process solid wastes varies due to the range of available landfill designs. Uncontained landfills can release contaminants into infiltrating surface water or groundwater or via wind and surface erosion (Evanko and Dzombak, 1997).

2.1.3 Sludges

The composition of sludges depends on the original waste stream and the process from which it was derived. Sludges resulting from a uniform waste-stream, such as wastewater treatment sludges, are typically more homogeneous and have more uniform matrix characteristics. Sludge pits, on the other hand, often contain a mixture of wastes that have been aged and weathered, causing a variety of reactions to occur. Sludge pits often require some form of pre-treatment before wastes can be treated or recycled (Smith et al., 1995).

2.1.4 Soils and Ground-Water Contamination

Soil consists of a mixture of weathered minerals and varying amounts of organic matter. Soils can be contaminated as a result of erosion/deposition from other contaminated soils or spills/direct contact with contaminated waste streams such as airborne emissions, process solid wastes, sludges, or leachate from waste materials.

Groundwater can be contaminated with metals directly by infiltration of leachate from land disposal of solid wastes, liquid sewage or sewage sludge, leachate from mine tailings and other mining wastes, deep-well disposal of liquid wastes, seepage from industrial waste lagoons, or from other spills and leaks from industrial metal processing facilities (e.g., steel plants, plating shops, etc.).

A variety of reactions may occur which influence the speciation and mobility of metal contaminants including acid/base, precipitation/dissolution, oxidation/reduction, sorption or ion exchange. Precipitation, sorption, and ion exchange reactions can retard the movement of metals in groundwater. The rate and extent of these reactions will depend on factors such as pH, complexation with other dissolved constituents, sorption and ion exchange capacity of the geological materials. (Evanko and Dzombak, 1997).

2.2 Remediation Technologies

Several remediation technologies are currently available for contaminated soils clean up. However, no one particular technology or process is usually appropriate for all contaminant types, their distribution and/or the physical, chemical and in some cases biological properties of the media to be treated.

Generally, remediation methods whether fully developed or emerging, are classified into two broad categories:

- Ex-situ – where the soil is removed from the ground for treatment, and
- In-situ – where the contaminated soil is treated while it remains in place in the ground.

The following sub sections briefly give some of the site restoration technologies that have been used in the remediation of contaminated sites in Europe. The advantages and disadvantages of each method are given. The disadvantages refer to process considerations which may limit broad use of the technology. An overview of the treatment technologies is then presented at the end of this section.

2.2.1 Ex-situ Treatment

The main aim of these methods is to remove the pollution from the site. The process involves the treatment or disposal of materials excavated from the ground. This clean up approach is important because it offers a once and for all ultimate solution, even though there will often be an associated waste stream to dispose of.

2.2.1.1 *Dig and Dump*

This physical method involves excavation of contaminated soil, taking it to a suitably licensed tip and filling the void with clean soil. It can be used to remove soil from the entire site, or just the soil from the worst spots.

This method does not treat the contamination, but relocates it to a controlled disposal point. Therefore, the method does eliminate all contaminants from the ground, for all time, at one go.

Dig and dump may be the most technically satisfactory remediation solution when the contamination is fairly shallow and the earthworks volumes are relatively small. The great advantage is that the facilities are carefully managed to give a high degree of control over the clean-up process and also to prevent the occurrence of further pollution events arising from the clean-up process itself. However, there are various drawbacks with the technique:

- The problem of contamination is not permanently destroyed of but simply transferred from one place to another.
- Transporting contaminated material through town and countryside could cause considerable environmental impacts, including odours, contaminated dusts, spillage, noise, etc, thus causing extra risk to workers and the public.
- If the site is contaminated to considerable depths, the cost of excavation and earth moving such volumes is prohibitive.
- If the water table is above the bottom of the excavation there may be a major influx of water into the site, and this will have to be contained, removed and treated.
- In addition, the excavated soil requires disposal at specific licensed sites at a cost (landfill tax).
- These landfill sites take up a lot of space and are quite unpopular.

According to an unpublished report, by the Institute for Environmental Health (IEH), for the Department of Health, landfill is the most common system of disposal in the UK for both domestic and industrial waste (Department of Health, 2002). About 85% of national waste is deposited in this way.

Fielder et al., (2000) assessed the impact on the health of residents living near the Nant-y-Gwyddon landfill site, in South Wales. Congenital abnormalities, reproductive health and other illnesses were reviewed. It was found that there were slight increases in congenital abnormalities for pregnant women living near the landfill site. Several chemicals were found to be emitted from the site. Their research found this to be consistent with increased complaints of headaches, eye-irritation and sore throats.

Multi site studies were conducted and published in March 2000 by the London School of Hygiene and Tropical Medicine (UK) on the health effects in relation to landfill sites (Martine, 2000). Increases in risk of adverse health effects like; low birth weight, leukaemia, birth defects, certain types of cancers, miscarriages, skin irritations, infant mortality, etc. were reported near individual landfill sites. Although biases and confounding factors cannot be excluded as explanations for these findings, they raise special concern and may indicate real risks associated with residence near certain landfill sites.

2.2.1.2 Thermal Treatment

Thermal treatment methods use heat to remove or destroy contaminants. They have long been recognised as an applicable *ex situ* technology for permanently and completely removing toxic organic compounds. The methods are particularly suitable for eliminating hydrocarbons.

Figure 2.1 below shows a generalised flowchart for thermal processes.

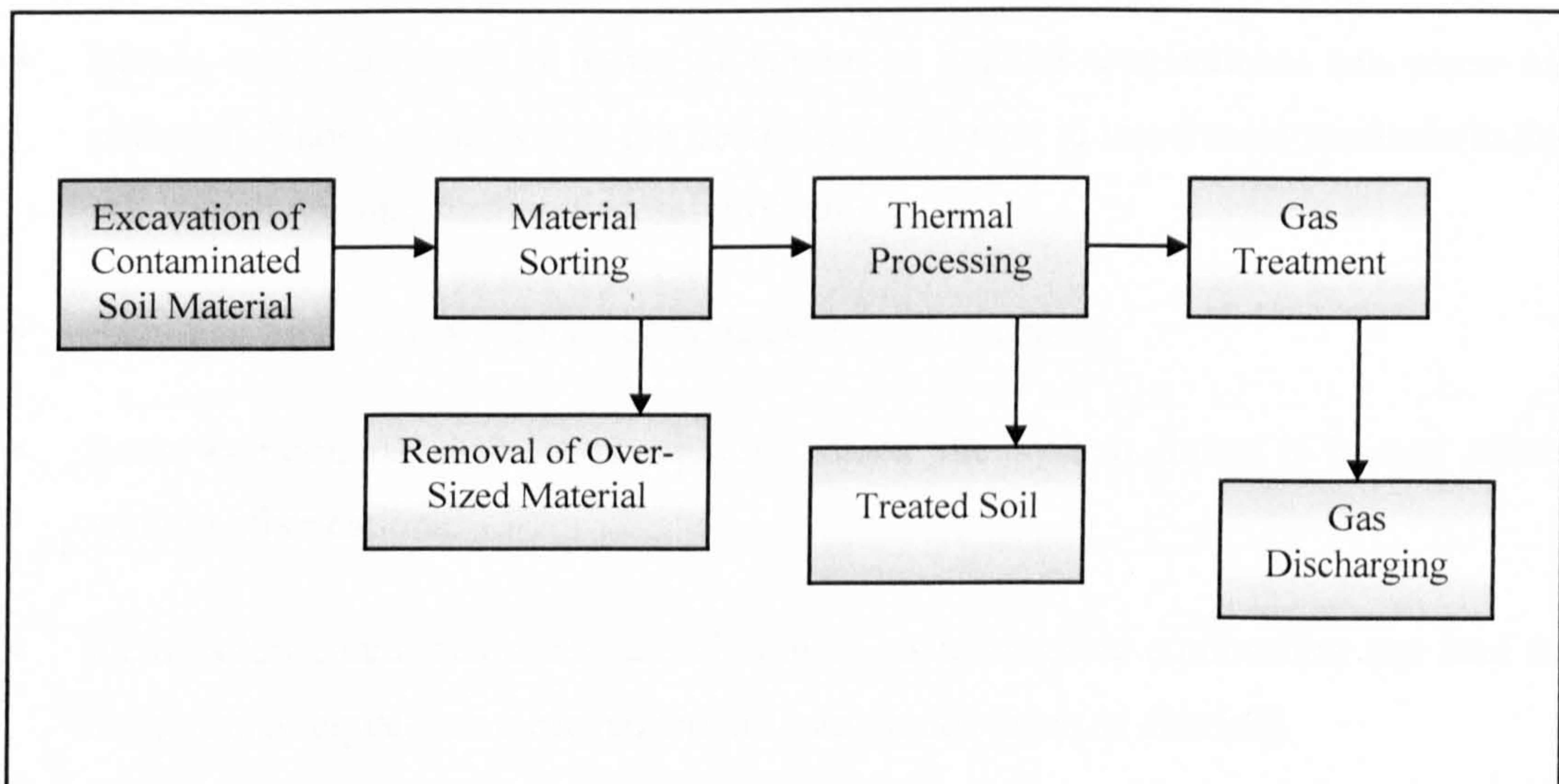


Fig 2.1 Flowchart Diagram for Thermal Cleaning of Soil

Thermal processes can be divided into two main categories: one-stage and two-stage systems (Pratt, 1994). One-stage systems destroy the toxic organic compounds directly within the contaminated soil or substance. End products of this incineration are bottom ash (normally returned to the original site for backfilling or discharged to landfill) and gaseous emissions. Two-stage systems use volatilisation and/or pyrolysis to convert the toxic compounds into the gaseous phase, with subsequent thermal combustion of the gaseous products or condensation of the gaseous inorganic compounds.

With this technique, emission controls are required, both of the gases and vapours produced by the furnace and of the quenching water which also becomes contaminated in the process.

Thermal systems can treat almost any type of contaminated soil, although soils with high clay and water contents require higher energy input and long residence times and are more difficult to handle (Sarsby, 2000).

The technology limitations include:

- Coarse soils (e.g. sandy, silty, etc.) respond best to thermal processes. Fine grained soils, especially those rich in clay, tend to form nodules in the rotary kiln during operation, consequently, reduce the efficiency of the process.
- Metals which disperse in fumes or vapour at applied temperatures can cause air pollution. Those remaining in the treated material tend to leave toxic residuals in the ash, thereby posing further disposal problems.
- Resulting high or low pH may corrode system components.
- Some compounds such as phosphorus attack the system lining if burned alone without other cations.
- Incineration conditions need careful control, as incomplete combustion can lead to formation of equally or more hazardous compounds (such as dioxins).

2.2.1.3 Vapour Extraction/Steam/Air Stripping

A phase change is initiated in contaminated solids or liquids by providing a source of energy (e.g. steam). Volatile contaminants are then vapourised and removed.

The treatment procedure involves withdrawing the contaminated material and placing it in a closed system (e.g. a distillation column). Steam, heat and/or a vacuum are then applied to facilitate volatilisation. The closed treatment system does not release contaminants into the atmosphere.

The principal considerations for the successful application of this process are the volatility of organic compounds and the porosity or looseness of the contaminated material.

The disadvantages of this method include:

- Volatilization is inhibited by high humic content of soil.
- Technology is best suited for relatively permeable, homogeneous soils.
- Residual liquid from treated air requires disposal.
- Remediation may take many years.
- Heavier molecular weight contaminants, such as hexachlorobenzene, may present some difficulty in application for this technology (TABs, 2002).

2.2.1.4 Carbon Adsorption

In this chemical *ex situ* process the contaminant liquid is directed into a closed system containing a reactor column composed of beds of activated charcoal or fluidized bed. Fixed or moving bed adsorption systems are used in reactor columns where the contaminant liquid moves upward or downward by gravity or under pressure through beds of activated carbon, where the contaminant is adsorbed and thus removed from the liquid.

In a fluidised bed operation, contaminated liquids move upward through a bed of activated charcoal which has been placed in suspension under the upward gradient of

the pressurised fluid. Thus optimum surface area of the carbon particles is made available to come into contact with the contaminated material for more efficient adsorption.

The process is an efficient one, requiring approximately 1kg of carbon per 6,000 litres of liquid to be treated. The adsorptivity is controlled by the pH, alkalinity or acidity of the compounds being treated (amines are adsorbed more efficiently in an alkaline environment, while organic acids favour acidic conditions). It is most effective in removing high molecular weight compounds and moderately effective in adsorption of chlorinated solvents. It is easy to implement, does not create air emission problems, but does, produce hazardous waste which has to be disposed of.

2.2.1.5 *Bioremediation*

Bioremediation is the process of using micro-organisms to destroy contaminants or to convert them to non-hazardous end products such as water and carbondioxide. The system is relatively ineffective with inorganic compounds and metals.

The system involves creating an aqueous slurry by combining the contaminated soil, sediment, or sludge with water and other additives. The micro-organism population is obtained either by adding adapted toxicant-degrading micro-organisms to the slurry or by injecting nutrients into the slurry to stimulate the growth of the indigenous micro-organisms. The slurry is then mixed to keep solids suspended and micro-organisms in contact with the soil contaminants. Upon completion of the process, the slurry is dewatered and the treated soil is disposed of.

Almost all organic compounds and some inorganic compounds can be degraded biologically if sufficient time and proper physical and chemical conditions are provided. In order to achieve an efficient biological degradation, the presence of the following conditions is paramount:

- Nutrients,
- Sufficient water,
- Appropriate organisms,
- Favourable temperature.

- Sufficient oxygen for aerobic processes and full depletion of oxygen for anaerobic processes,
- Concentrations which are non-toxic to the micro-organisms,
- Sufficient contaminants for the micro-organisms,

Some of the drawbacks of this technology include:

- Completing treatment can take over 6 months. Consequently, handling large amounts of soil over a long period of time can be expensive.
- The method requires a relatively large area for operation.
- Because of its biological nature, bioremediation is rarely suitable for treatment of soils with excessive concentrations of heavy metals, chlorinated organics, some pesticides/herbicides or inorganic salts (US EPA, 1991). Microbial degradation is inhibited by heavy metals and complex organic compounds.

2.2.1.6 Solidification/Stabilisation

These methods (also referred to as immobilization methods) change the physical and chemical characteristics of the waste in order to reduce the availability of contaminants to potential targets. The strategy for treatment, therefore, involves controlling the source of contaminated materials by either fixing the contaminant in a structurally stable matrix or immobilising it by chemical reaction and pH modification, or by encapsulating it in a solid matrix. The techniques are therefore not intended to remove the contaminants from the soil, but rather to eliminate physically or chemically the toxicity and/or mobility of the hazardous substances within the soil, which can then be left in place or handled in a safe way.

Solidification involves adding reagents to the waste material to form an inert mass, while stabilisation involves adding chemicals to the contaminated material to convert it to an inert form. Both methods produce a tightly formed solid matrix that resists degradation and leaching. And in practice, many commercial systems and applications involve a combination of the two processes (CIRIA, 1995a)

Ex-situ solidification is done either on or off-site, where the material is removed and mixed in specifically designed, often patented and proprietary equipment. After

mixing, the mixture is transported or dumped to a landfill for placement and solidification. The processes are accomplished by mixing the solid or semi-solid waste, usually with a combination of portland cement, lime, fly ash, calcium chloride, bentonite, and other reagents and surfactants to facilitate mixing and setting of the mixtures.

Solidification/stabilisation techniques are applicable to heavy metals and organic contaminants, either solid, sludge or liquid forms (US EPA, 1993). The binding agents are typically inorganic materials such as cement, fly ash, pozzolans and silicates, although organic materials such as asphalt, epoxy resins and polyesters have been used.

The benefits of solidification/stabilisation are that where such materials are placed in a landfill on site, the land still remains useful, the solidified material more often is relatively impervious, and it has dimensional stability and durability against natural destructive forces.

The disadvantages of this technique include:

- Because the contaminants are not permanently destroyed or removed, the treated soil still forms a potential source of hazard. Long-term monitoring may be required.
- The presence of combinations of different compounds can sometimes mean that no adequate overall solidification/stabilization technique can be found.
- The provision of a sufficient degree of mixing or contact between the contaminants and the treatment agent presents a fundamental and difficult problem in the general case of multiple-constituent wastes intermixed with soil of different textures and permeabilities.
- Volume of contaminated material can increase 50 to 100% due to addition of solidifying agents.
- Weathering and ageing may reduce the stabilising effect, and leachability may be increased by freeze-thaw cycles.

2.2.1.7 Soil Washing

Soil washing is a water-based process treating soils *ex situ* using selected designed solvents to remove contaminants, (Anderson, 1993). It employs chemical and physical extraction and separation techniques to remove organic, inorganic and radioactive contaminants (including mixtures) from soils, sediments and similar materials. The process is applicable to media contaminated with a wide variety of heavy metal, radionuclides, and toxic organics including herbicides, pesticides, PAHs and PCBs (Mugglestone and Hughes, 1994). Typically, the technology is most effective with coarse-grained soils than fine grained soils. A schematic flow diagram of a typical soil washing process is given in Figure 2.2.

Soil washing is accomplished by bringing the contaminated soil into contact with a wash solution, separating the soil and solution, and treating the solution. The solution is brought into contact with the soil and vigorously agitated to transfer contaminants into the wash solution. The process removes contaminants from soils by dissolving or suspending them in the wash solution (which is later treated by conventional wastewater treatment methods). Surfactants or similar solvents are often used to improve the removal of petroleum hydrocarbons and a wide variety of other organic contaminants from soils (NFESC, 2002).

Soil washing typically incorporates particle size separation, gravity separation, and attrition scrubbing techniques during washing (Deuren et al., 2002). The concept of using particle size separation to reduce the amount of solids requiring treatment is based on the tendency of many organic and inorganic contaminants to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion. Washing separates fine clay and silt particles from the coarser sand and gravel soil particles, effectively separating and concentrating the contaminants into a smaller volume of soil consisting of the clay and silt fraction. This fraction can then be treated further or disposed of. Gravity separation is effective for removing high or low specific gravity particles such as heavy metal-containing compounds (lead, radium oxide, etc.). Attrition scrubbing removes adherent contaminant films from coarser particles. However, attrition washing can increase the fines in soils processed. The

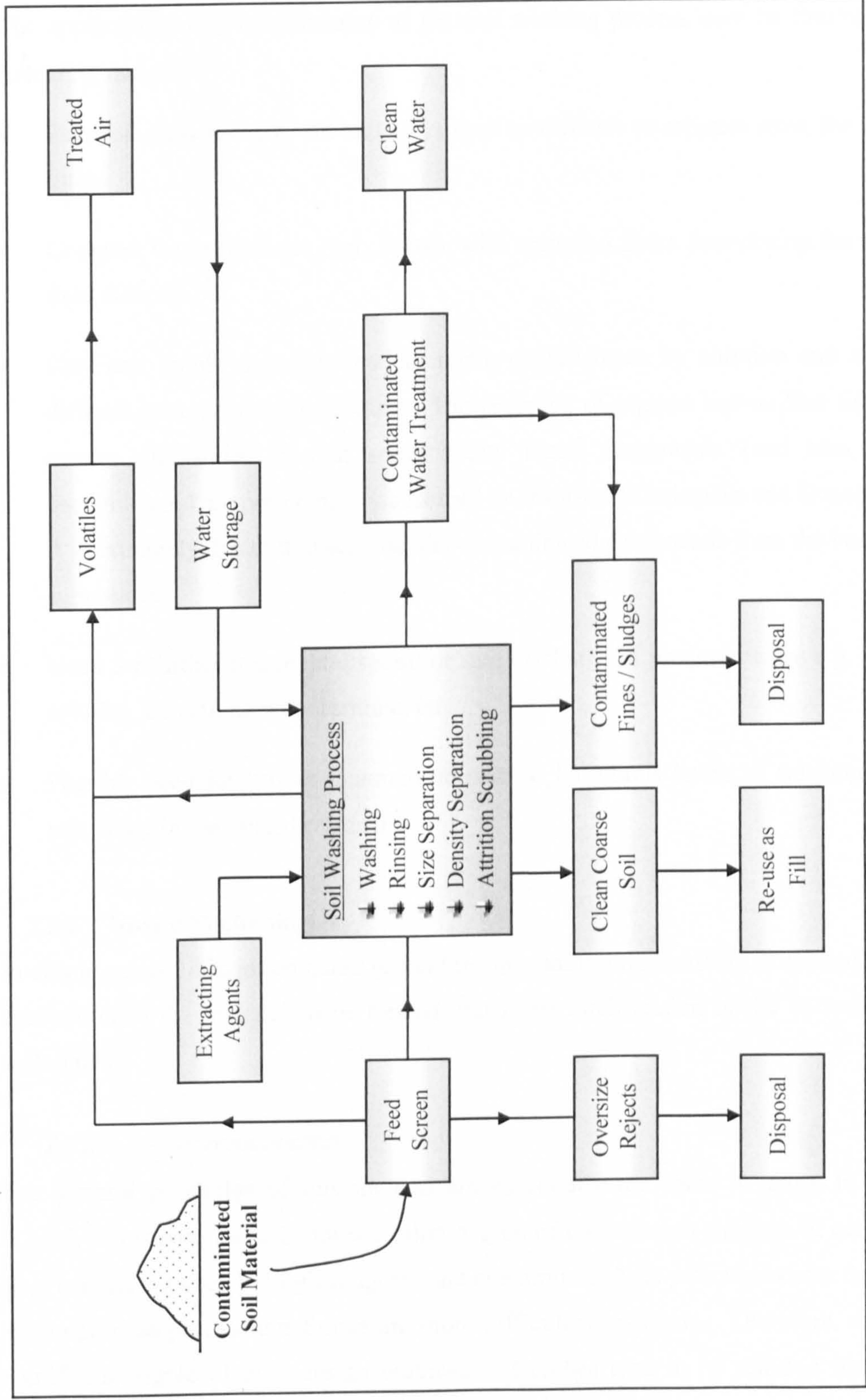


Fig 2.2 Flowchart Diagram of a Typical Soil Washing Process, (After CIRIA, 1995a)

cleaned sand and gravel fraction can be returned to the site for re use as fill.

The applicability and effectiveness of the soil washing process may be limited by the following factors:

- Fine soil particles (e.g. silt and clay) may be difficult to separate from the washing fluid.
- Complex waste mixtures (e.g., metals with organics) make formulating the washing fluid difficult.
- Clay and humic materials tend to retain contaminants by sorption and often are difficult to treat by soil washing. The presence of organic humus like substances creates difficulties in that some heavy metal compounds (and also organic contaminants) are preferentially adsorbed or absorbed (Kuziemska and Quanta 1998). It is extremely difficult to separate the contaminated compounds from the humus like substances.
- Need for further treatment/disposal or safe discharge of process wastes e.g. washing solution, contaminant concentrate, etc.
- Possible need for further treatment to address hazardous levels of washing solvent remaining in the treated residuals.

2.2.2 In-situ Technologies

In-situ treatment of contaminated ground means that the remediation is applied without excavation of the material to be treated, but some modification of the contaminant is undertaken.

2.2.2.1 *Bioremediation*

The general principles of this method are essentially the same as those in Section 2.2.1.5. However, there is not the same degree of control over processing conditions, (e.g. contact between biological agents and contaminants), as with the ex-situ treatment. Also optimum process conditions are more difficult to maintain. Therefore, there is a significant degree of over design required. Microbes tend to be selected from those types occurring naturally on the site and which are therefore tolerant to the prevailing conditions.

Factors influencing the decision of whether or not to use in situ remediation are:

- Soil structure and hydrogeology – permeabilities (horizontal and vertical), organic carbon content,
- Microbiology – bacterial counts, enrichment cultures,
- Contamination – type of contaminants and concentration levels, free floating layers.

The drawbacks of this method include (TABs, 2002):

- The process can take a considerable period of time (typically 6 months to 2 years) and would therefore not be suitable for land that has to be developed rapidly (Taylor and McLean, 1992).
- Not effective at sites with high concentrations of heavy metals, inorganic salts, or chlorinated organics. High concentrations of these compounds are likely to be toxic to micro-organisms. Method not suitable for treatment of inorganic contamination.
- Contaminant mobility may increase due to microbe enhancement.
- Not effective in highly layered, clay, or bedrock sub-surfaces.

2.2.2.2 *Solidification/Stabilisation*

Solidification/Stabilisation in-situ treatment is/are designed to eliminate the mobility and/or toxicity of contaminants within the ground through both physical and chemical means (refer to Section 2.2.1.6).

In-situ operations involve mixing soil with a binder, (such as Portland cement) to reduce contaminant mobility by a combination of physical entrapment (e.g., encapsulation or porosity reduction) and chemical reaction (e.g., hydroxide precipitation). The techniques use auger systems or grout injection equipment to apply solidifying/stabilising agents to the ground soils.

Auger mixing involves using large soil augers to mix binder into in situ soil. Binder is applied through nozzles at the bottom on the augers as they turn, mixing and drilling into the soil. Grout injection involves forcing binder into the soil porosity using high-pressure grout injection pipes forced into the soil. Figure 2.3 shows a typical auger and injector system during stabilisation/solidification.

The following factors may limit the applicability and effectiveness of the process:

- A high proportion of rocks or debris in situ can interfere with binder injection or mixing.
- Depth of contaminants may limit some types of application processes.
- Future usage of the site may "weather" the materials and affect ability to maintain immobilization of contaminants.
- Long-term effectiveness has not yet been demonstrated for many contaminant/process combinations.
- The solidified material may hinder future use of the site.
- Reagent delivery and effective mixing are more difficult and costly than for ex-situ applications.
- Binder injection and mixing must be controlled to minimize the spread of contaminants to clean areas.

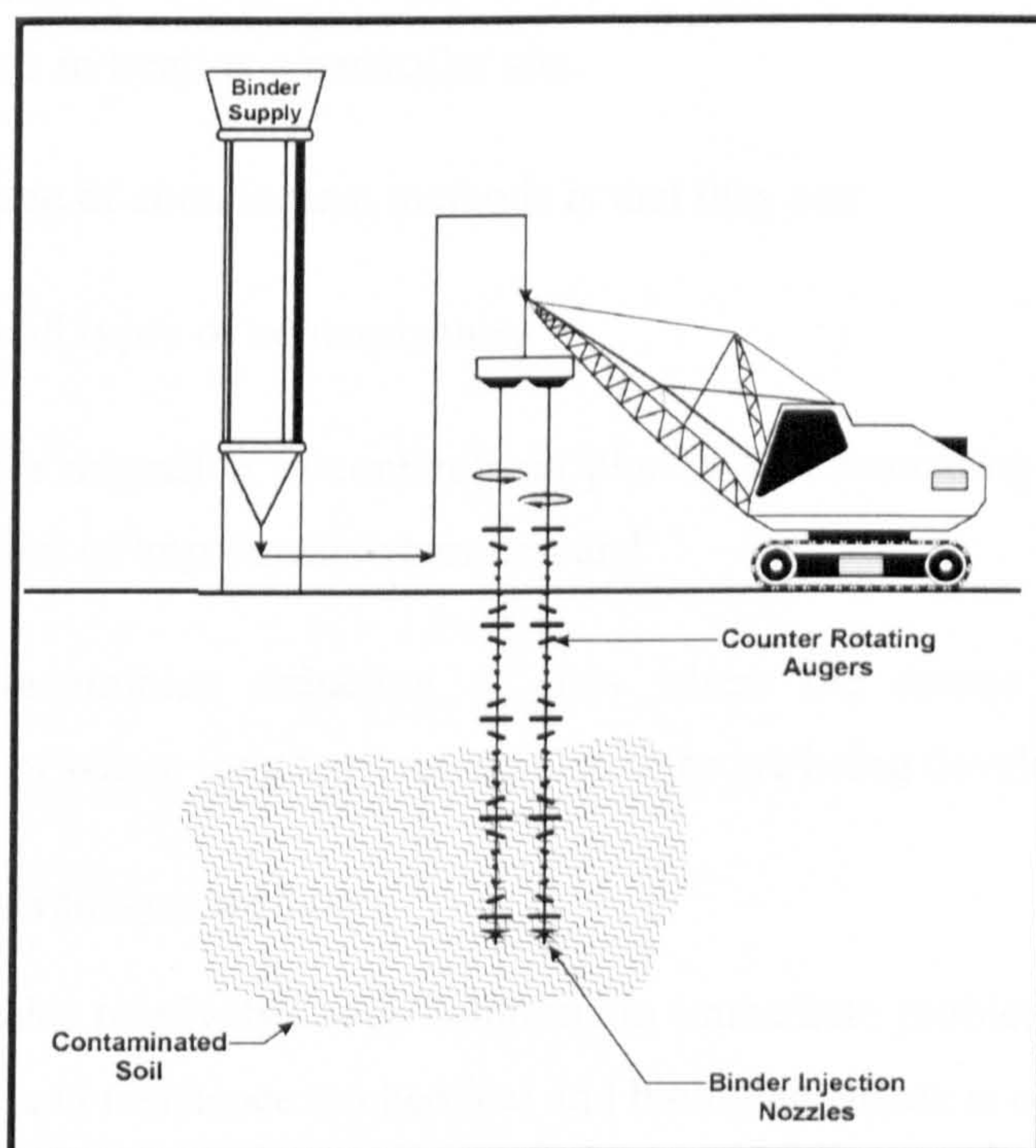


Fig 2.3 Typical Auger and Binder Injector System at Work

- Exposure to water or freeze/thaw cycles may reduce immobilization of contaminants.
- It can be difficult to formulate an effective binder for complex waste.

2.2.2.3 *Containment*

Containment (encapsulation) measures are often performed to prevent, or significantly reduce, the migration of contaminants in soils or ground water. Containment is necessary whenever contaminated materials are to be buried or left in place at a site. In general, this type of approach is performed when extensive subsurface contamination at a site precludes excavation and removal of wastes because of potential hazards and/or unrealistic cost. It is also undertaken if the available clean-up techniques are so slow that the pollution would spread by an unacceptable amount during a clean-up process.

Containment involves constructing physical barriers around or beside the contaminated ground. Consequently, components of containment systems are horizontal cover layers (over the pollution), vertical barriers (around the pollution) – as shown in Figure 2.4 and horizontal bases (beneath the pollution). It may, in some circumstances, be necessary to use all components in treating a particular site.

The main advantage of containment methods is that they can:

- be applied to all types of contaminants,
- prevent further migration of contaminant plumes to surrounding site areas through the construction of impermeable barriers, and
- allow for contaminant reduction at sites where the source is undetermined, inaccessible, or where long term remedial actions are being developed.

However, its disadvantages include:

- System provides relatively cheap solutions to immediate problems, but their long-term stability and resistance to chemical and biological attack is often questionable.
- Forces generated by expansion, contraction, land slippage and changing groundwater pressures also limit their long-term effectiveness.
- There is potential for the barrier walls to degrade or deteriorate over time.

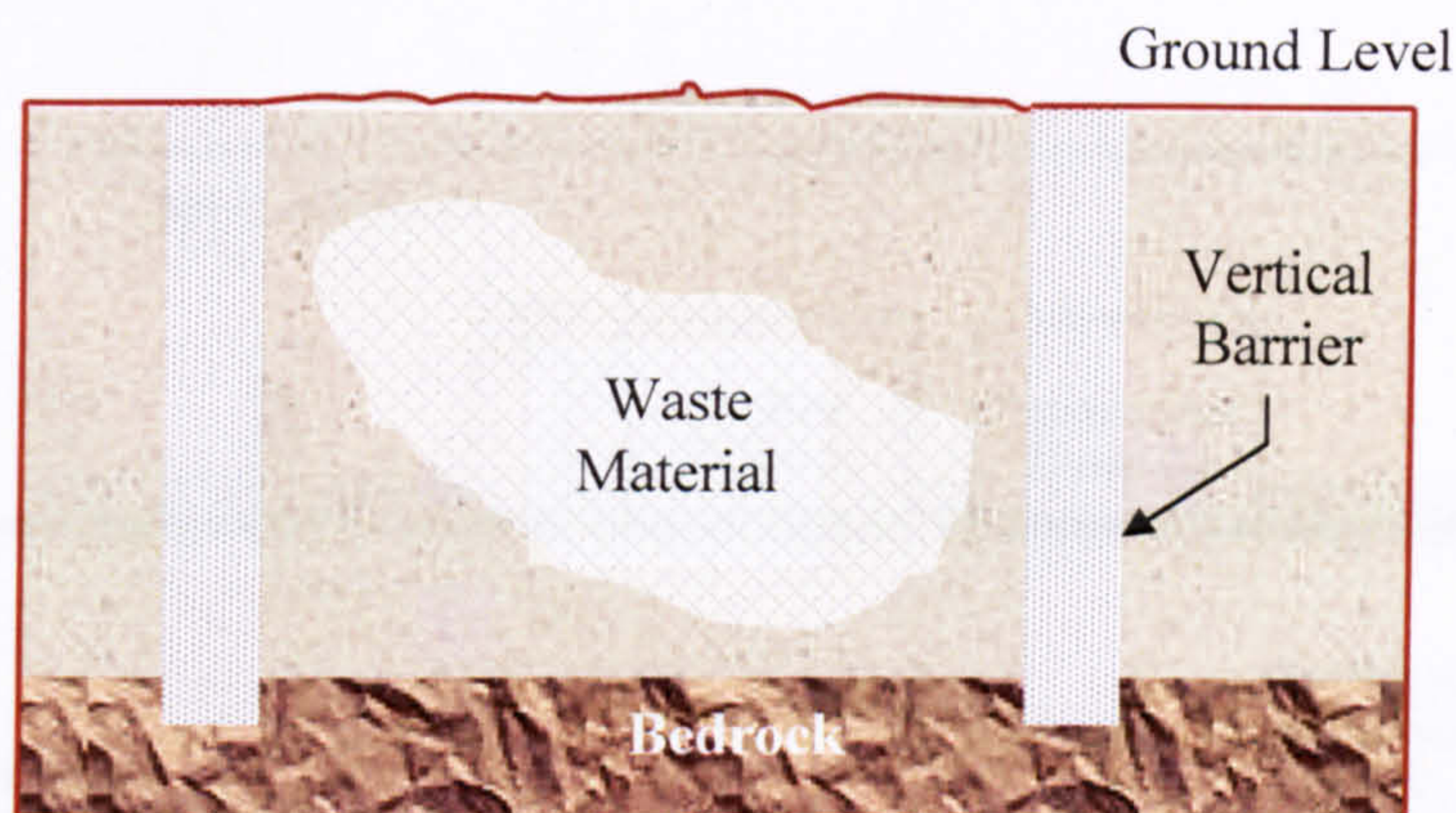


Fig 2.4 Sketch Showing Physical Barriers used to Contain Waste Material

2.2.2.4 Soil Flushing

In-situ soil flushing is designed to physically remove contaminants from soils in the saturated zone or near surface saturated zone (CIRIA, 1995b). Water, or water containing additives to enhance contaminant solubility and mobilisation, infiltrates into the soil (using e.g. sprinklers, vertical wells, infiltration trenches, horizontal in ground pipes, etc.) or is injected into the ground water to raise the water table into the contaminated soil zone. Contaminants are leached into the ground water, which is then extracted using pump-and-treat methods.

Recovered ground water and flushing fluids with the desorbed contaminants are treated prior to recycle or release to local, publicly owned wastewater treatment works or receiving streams. To the maximum extent practical, recovered fluids are reused in the flushing process. The separation of surfactants from recovered flushing fluid, for reuse in the process, is a major factor in the cost of soil flushing. Treatment of the recovered fluids results in process sludges and residual solids which must be appropriately treated before disposal. Air emissions of volatile contaminants from recovered flushing fluids are also collected and treated, as appropriate, to meet applicable regulatory standards. A typical soil flushing system is shown in Figure 2.5 below.

The target contaminant group for soil flushing is inorganics including radioactive contaminants. The technology can be used to treat volatile organic compounds (VOCs), fuels, and pesticides. The technology also offers the potential for recovery of metals and can mobilize a wide range of organic and inorganic contaminants from coarse-grained soils (Deuren et al., 2002).

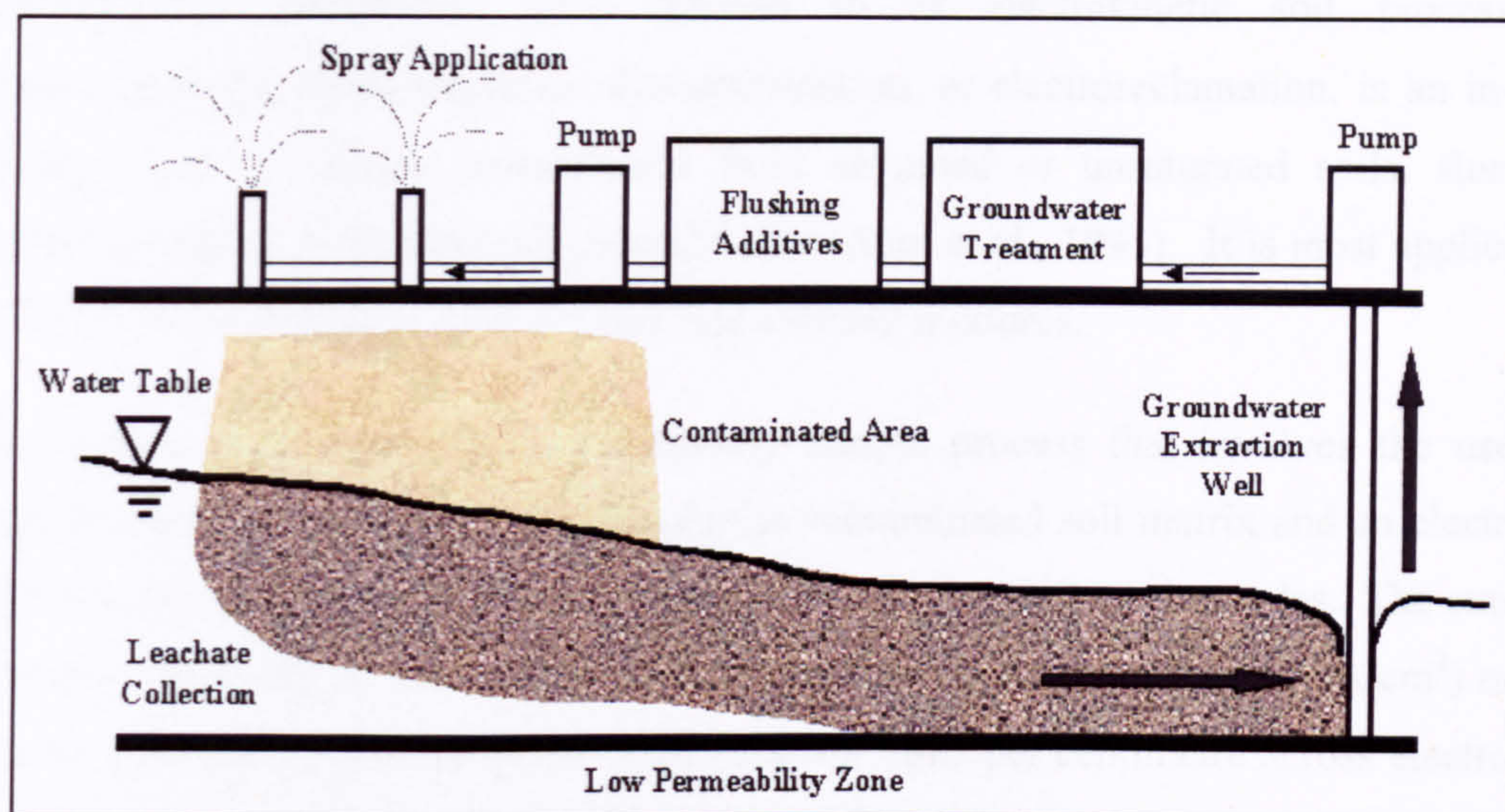


Fig 2.5 Typical Soil Flushing System (after FRTR, 2003)

The treatment method has the following limitations:

- Low permeability or heterogeneous soils (such as clays etc.) are difficult to treat.
- Surfactants are rendered ineffective by hard water.
- Surfactants can adhere to soil and reduce effective soil porosity.
- The flushing solution may alter the physical/chemical properties of the soil system. These alterations may affect operational efficiency (e.g. changes in permeability).
- Reactions of flushing fluids with soil can reduce contaminant mobility.
- The potential of washing the contaminant beyond the capture zone and the introduction of surfactants to the subsurface concern regulators. The technology should be used only where flushed contaminants and soil flushing fluid can be contained and recaptured.

2.2.2.5 *Electrokinetic Remediation*

Electrokinetic remediation, also referred to as electrokinetic soil processing, electromigration, electrochemical decontamination, or electroreclamation, is an in-situ process used to extract contaminants from saturated or unsaturated soils, slurries, marine dredging, sediments and ground water (Acar et al., 1995). It is most applicable in low permeability soils such as clays and silt-clay mixtures.

The technique is conceptually a relatively simple process that involves the use of electrode pairs. These are placed across the contaminated soil matrix and an electrical field is created by applying a low-voltage direct current (DC) to electrodes. The current density is generally of the order of milliamperes per square centimetre (mA/cm^2) or an electric potential difference of the order of a few volts per centimetre across electrodes placed in the ground (USAEC - ESTCP, 2000). As a result, one of the electrodes becomes the anode while the other becomes the cathode as shown in Figure 2.6. The movement of ions within the soil pore fluid completes the circuit. The current through the contaminated soil mass then leads to a number of phenomena that form the basis of the usefulness of this technology. Positively charged ions and particles move to the cathode with negatively charged ones heading to the anode. The concentration of the ions and/or particles in the neighbourhood of the electrode wells set the opportunity of extracting them from the site by e.g. through pumping them out. Surfactants and complexing agents can be used to increase solubility and assist in the movement of the contaminant. Also, reagents may be introduced at the electrodes to enhance contaminant removal rates. The detailed fundamental phenomenon is explained in sections later in this chapter.

The growing list of contaminants affected by the electrokinetic process includes (van Cauwenberghe, 1997):

- Heavy metals (lead, mercury, cadmium, nickel, copper, zinc, chromium);
- Radioactive species (Cs_{137} , Sr_{90} , Co_{60} , Ur);
- Petroleum hydrocarbons (diesel fuel, gasoline, kerosene and lubricating oils);
- Explosives; and
- Mixed organic/ionic contaminants.

This, therefore, makes electrokinetics a potential multi contaminant soil cleaning technology.

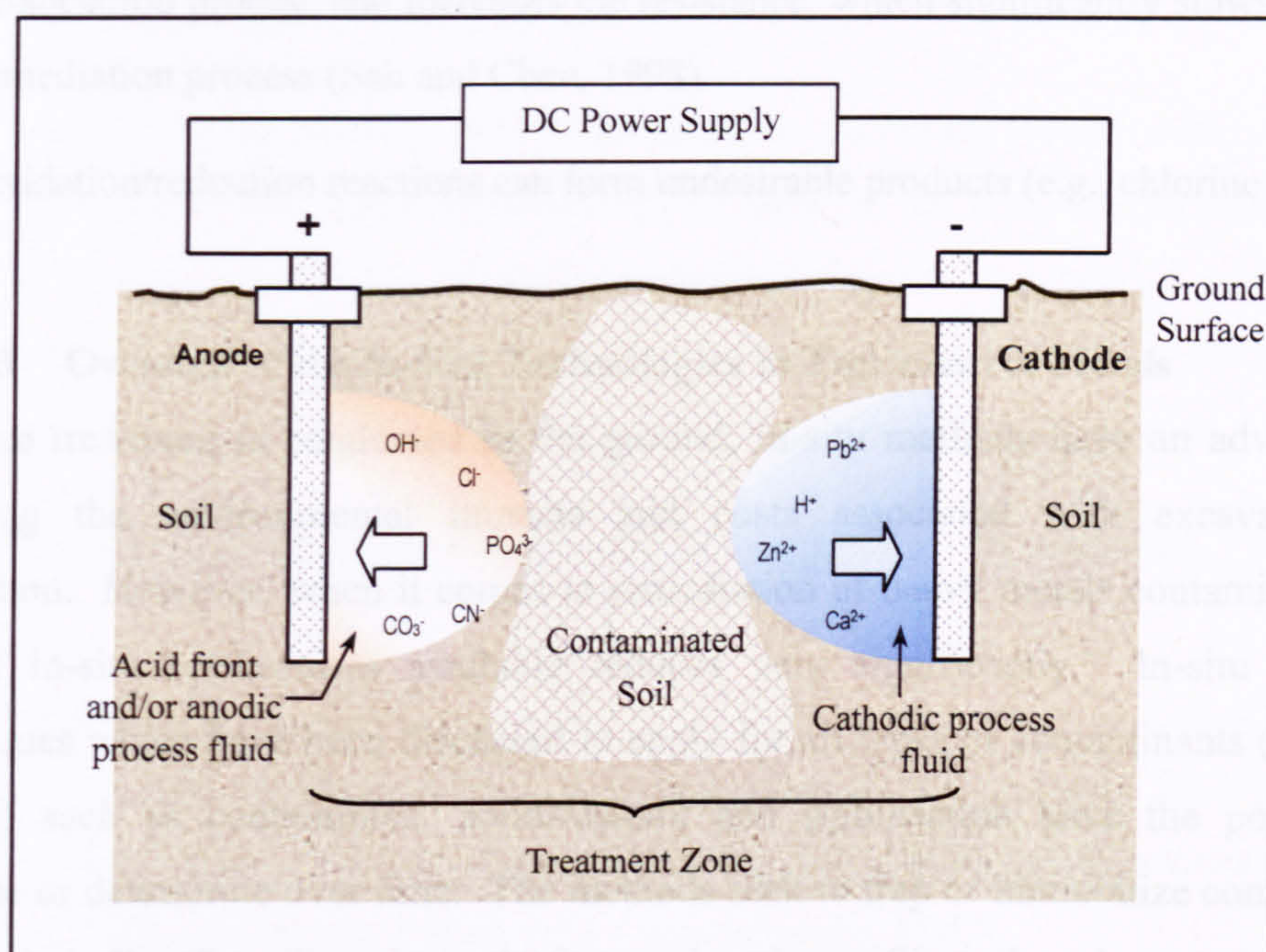


Fig 2.6 General Schematic of Electrokinetic Remediation

Factors that may limit the applicability and effectiveness of this process include:

- Effectiveness is sharply reduced for wastes with a water content of less than 10 percent.
- The presence of buried electro conductive material in the ground such as metals and ores interfere with the electro processes and cause inefficiency in the technique.
- Metallic electrodes dissolve as a result of electrolysis and introduce corrosive products into the soil mass.
- Electrokinetics is most effective in clays because of the negative surface charge of clay particles. However, the surface charge of the clay is altered by both changes in the pH of the pore fluid and the adsorption of contaminants. Extreme pH at the electrodes and reduction-oxidation changes induced by the process electrode

reactions many inhibit electrokinetic effectiveness, although acidic conditions (i.e., low pH) may help to remove metals. (Deuren et al., 2002).

- The surface of the electrode attracts the gas generated from the electrolytic dissociation process and increases the resistance, which significantly slows down the remediation process (Sah and Chen, 1998).
- Oxidation/reduction reactions can form undesirable products (e.g., chlorine gas).

2.2.3 Overview of the In-Situ Technologies in Treatment of Metals

Because treatment is conducted in the ground, in-situ methods have an advantage of avoiding the environmental impacts and costs associated with excavation and extraction. However, when it comes to remediation of heavy metals contaminants, the list of in-situ applications available reduces very significantly. In-situ clean up techniques which have been discussed to apply for all types of contaminants (including metals) such as containment, solidification and stabilisation have the potential to degrade or deteriorate over time. The methods seek to trap or immobilize contaminants within their "host" medium instead of removing them. Since they do not permanently treat or remove metal pollutants from the soil, they leave a potential source of future hazard. Use of such technology does not guarantee that future remediation is not necessary.

Other methods such as barriers that prevent the further spread of contaminants may be effective remedies in cases where drinking water supplies are not endangered by the contamination. However, once a plume is identified and characterized, public pressure often demands that the offending source be removed or destroyed.

Other in-situ techniques which have been investigated and implemented before by the industry and researchers but have failed to demonstrate the ability to remove heavy metals from contaminated soils include bioremediation and thermal treatment, (Virkutyte, et al. 2002). Others, such as soil washing/flushing, have demonstrated potential effectiveness in removing heavy metals from the soil matrix. However, the methods cannot reduce their toxicity, (Ma et al., 1997).

Another major limitation of most of the in-situ decontamination technologies is that they are restricted to soils with relatively high permeabilities. Clay and other fine

grained soils pose three significant problems to any potential remediation technology (Alshawabkeh et al., 1999):

- (i) Low hydraulic conductivity that restricts the fluid volume flow rate making the soils non-responsive to traditional soil cleaning efforts.
- (ii) Large specific surface area that provides numerous active sites for surface reactions. The large specific surface area of the fine-grained soil provides numerous active sites for surface complexation and sorption of contaminants. These reactions reduce the quantity of contaminants in the dissolved phase and thus reduce the cleanup efficiency of most remediation technologies.
- (iii) many of these reactions are dynamic, pH dependent, and reversible.

Additionally, poor accessibility to the contaminants and difficulty in delivery of treatment reagents, thereby, makes many treatment processes (e.g. soil flushing, vapour extraction and pump-and-treat) rather ineffective when applied to low permeability soils present at many contaminated sites, (van Cauwenberghe, 1997).

Furthermore, recovery of ionic contaminants (such as metallic ions) from ground and groundwater is limited by the fact that soil is a powerful ion exchange media. Ionic contamination becomes adsorbed on soil particles following contact, (Lageman et al. 2004). Simple flushing action alone will not recover it, (van Cauwenberghe, 1997). A pH shift must be applied to desorb and mobilize the contaminants. However, flushing with strong acids usually destroys the basic soil structure, and may thus be self-limiting.

As none of the other in-situ soil remediation efforts have demonstrated the efficient removal of heavy metals, there is a necessity to develop other methods to remediate soil contaminated by heavy metals. Electrokinetic soil remediation, on the other hand, has attracted increased interest in the last decade as an emerging technology. This has mainly been due to its ability to treat a diverse range of contaminant species in both fine and coarse grained soils. Electrokinetics offers advantages over other technologies currently available for metals remediation, specifically (Geokinetics, 1998):

- Electrokinetics is an in-situ technology that has much less impact on existing landscaping, buildings or structures.
- Unlike acid and other flushing reagents, the process exploits induced localized pH alterations to mobilize metal ions so the soil matrix is not destroyed.
- The process is not limited by low soil permeability - It is most effective in low permeable soils (hydraulic conductivity $< 10^{-5}$ cm/s).
- The metals are actually removed from the soil unlike chemical stabilization, which incorporates metals into a compound with low solubility.

Electrokinetic remediation efficiency is however hampered by the limitations listed above in Section 2.2.2.5. Attempts of having various methods developed by combining this technique with others, for application in the remediation process, would be the key. One such method, which could be applied in conjunction with it, is soil flushing.

Currently, soil flushing has been applied to a limited range of metals, (Ma et al., 1997). The method requires consideration of the potential risk of aquifer contamination by residual flushing solution at the site. The permeability of the soil and the characteristics of the groundwater flow are the main site-specific considerations affecting its applicability.

Electrokinetics is most applicable to sites at which the soil is homogeneous and the moisture level is relatively high (Section 2.3.3.1). The technique primarily would require addition of water to maintain the electric current and facilitate migration. By combining the two processes, soil flushing would provide this water, while electrokinetics process would assist soil flushing by increasing the permeability or accessibility to the contaminants (especially in fine grained soils) as well as aiding movement of treatment agents into the soil. Table 2.2 shows an overview of the two in-situ remediation techniques as well as the proposed combined method. It is anticipated that the combined technology would provide further opportunities for improving the effectiveness of soils cleanup operations.

Table 2.2 Overview of the Proposed In situ Method for Remediation of Soils Contaminated with Heavy Metals

EVALUATION FACTOR	TECHNOLOGY		
	Soil Flushing	Electrokinetics	Combined Technology
Range of Metals Treated	Limited	Broad	Broad
Major Limiting Factor(s)	Potential contamination of the aquifer from residual flushing solution	Maintaining; <ul style="list-style-type: none">▪ Optimum moisture content▪ Contaminants in solution	Limited information about technology performance
Site Specific Considerations	<ul style="list-style-type: none">▪ Permeability of soil▪ Groundwater flow and depth	<ul style="list-style-type: none">▪ Homogeneity of soil▪ Moisture level in soil▪ Best in low permeability soils▪ Mixtures of species may not all become mobile at the same pH▪ Buried conductors and / or high conductivity soils reduce process efficiency	Buried conductors and / or high conductivity soils reduce process efficiency

2.3 Electrokinetics Technology

This section aims to describe in detail the electrokinetics process, the factors that affect its performance as well as the commercial electrokinetics remediation technologies available to date. An overview of these methods is presented at the end of the section.

2.3.1 Process Definitions

The principles behind electrokinetic remediation are those of the electrolytic cell where ions, in pore water surrounding the soil particles, migrate under the influence of electricity. Below are the definitions of the components of the electrolytic process:

Electrolyte: is a substance that dissociates in solution into positive and negative ions to produce an electrically conductive medium.

Electrolysis: the passage of an electric current through an electrolyte decomposing it in the process; negative ions (anions) are attracted to the anode, where they are oxidized (lose electrons). Positive ions (cations) are attracted to the cathode, where they are reduced (gain electrons).

Electrolytic Cell: a cell containing an electrolyte through which an externally generated electric current is passed by a system of electrodes in order to produce an electrochemical reaction (refer to Figure 2.7).

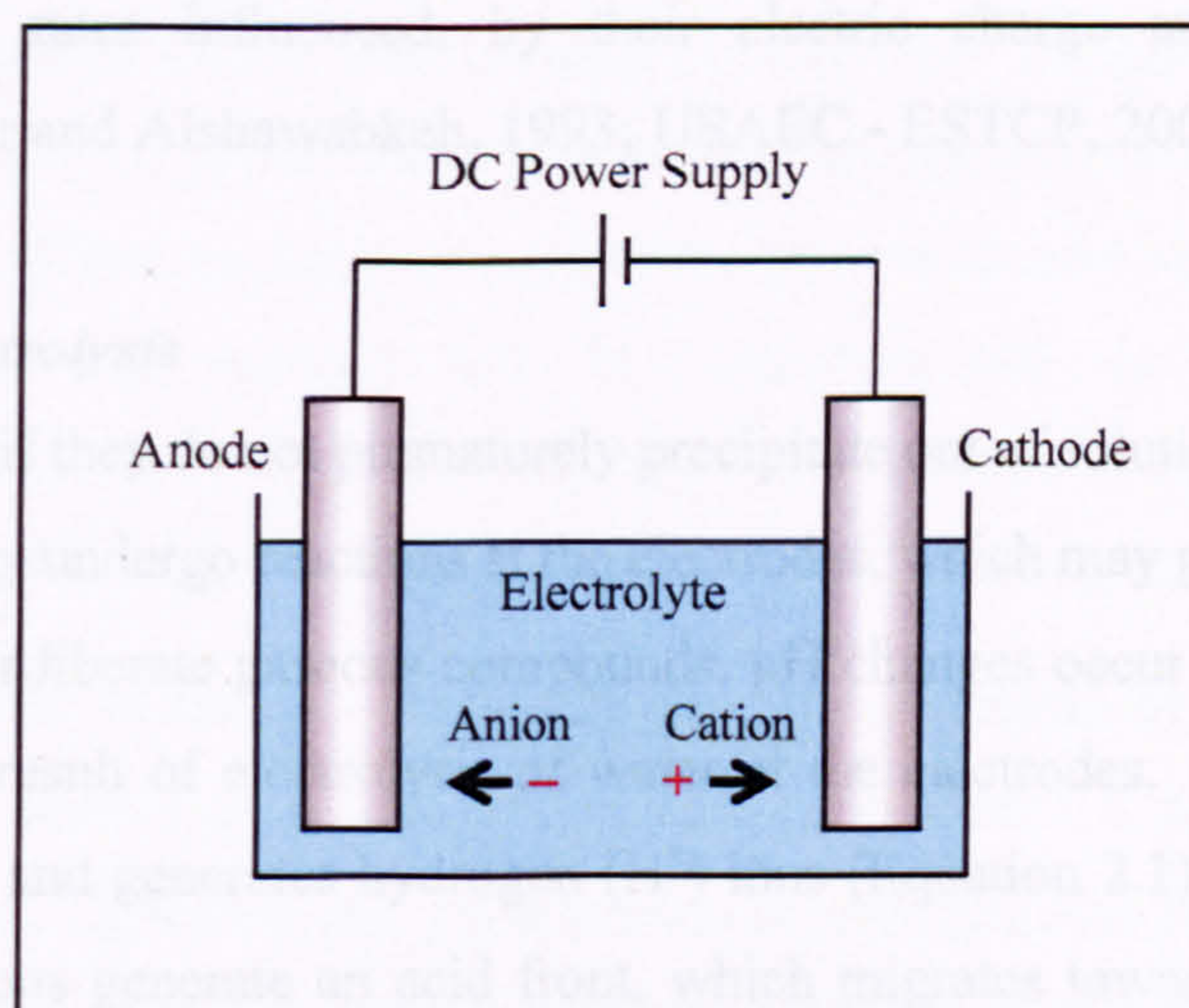


Fig 2.7 Electrolytic Cell

Electrode: Any terminal by which an electric current passes in or out of an electrolytic cell. The anode is the positive electrode and the cathode is the negative electrode.

Electrokinetics: is the movement of water (electroosmosis), ions and polar molecules (electromigration), and charged solid particles (electrophoresis) relative to one another between two electrodes under the action of an applied direct electric current.

2.3.2 Electrokinetic Phenomena

When a direct current is applied across two electrodes previously inserted between a saturated or partially saturated soil mass, an electrical field develops between the anode and cathode. The application of this electric field causes several effects on the soil solids, pore fluid, and contaminant behaviour (Acar and Alshawabkeh, 1993; Acar and Alshawabkeh, 1994; Mitchell, 1993; Yeung 1990; Yeung and Mitchell, 1993). These effects include electromigration, electroosmosis, changes in pH, and electrophoresis. Sections 2.3.2.1 to 2.3.2.4 discuss these processes in detail while the fundamental concepts of the technology are depicted in Figures 2.8 and 2.9.

2.3.2.1 Electromigration

Ions and polar molecules dissolved in the soil pore fluid migrate under an electric field. This movement of species relative to the movement of pore fluid is called electromigration (Figure 2.8a). Under the electric field, cations (positively charged ions) move towards the cathode whereas anions (negatively charged ions) move towards the anode at different rates influenced, by their electric charge and physicochemical characteristics (Acar and Alshawabkeh, 1993; USAEC - ESTCP, 2000).

2.3.2.2 Electrolysis

The migrating ions, if they do not prematurely precipitate out of solution, concentrate near the electrodes or may undergo reactions at the electrodes, which may plate the metals onto the electrodes and/or liberate gaseous compounds. pH changes occur under the influence of the current as a result of electrolysis of water at the electrodes. Oxidation of water occurs at the anode and generates hydrogen (H^+) ions (Equation 2.1), creating an acidic environment. H^+ ions generate an acid front, which migrates towards the cathode. In contrast, reduction of water occurs at the cathode and generates hydroxyl (OH^-) ions (Equation 2.2), creating an alkaline environment. OH^- ions migrate as a base front

towards the anode (Acar, et al. 1988; Acar and Alshawabkeh, 1993; Rodsand et al., 2000).



Studies by Reddy et al (1997) showed that soils with high buffering capacity, such as the glacial till, hinder the development of the acid front, which results in alkaline conditions throughout the soil during electrokinetic remediation. However, soils possessing low buffering capacity, such as kaolin and Na-montmorillonite, favour the development of the acid front which results in a distinct pH gradient with pH values varying from 2 near the anode to over 11 near the cathode. In the latter, the transport of the H^+ ions is approximately two times faster than the OH^- ions. Thus, the acid front moves at a greater rate than the base front (Acar and Alshawabkeh, 1993) causing the soil between the electrodes to be acidified. This acidification, results in solubilisation of contaminants due to desorption and dissolution of species from the soil. This is advantageous because once contaminants are present in ionic form in the soil pore fluid, they migrate to the electrode of opposite polarity under the applied electric field (electromigration) and/or via electroosmosis, leading to their extraction from the soil at the electrodes (Reddy and Shirani, 1997). The base front, on the other hand, promotes the precipitation of the metal ions near the cathode which hinders the mobility of the contaminants.

The dissolution of contaminants near the anode, and precipitation of the metal ions near the cathode, significantly affects the resulting pH and ionic strength of pore water, the mobility and solubility of metal contaminants, and charge conditions of soil particles. The variation of pH affects the ionic strength of the pore water and soil surface properties, such as cation exchange capacity and the magnitude and sign of zeta potential. Furthermore, speciation, mobility and solubility of contaminants are often varied with pH in soils during treatment, which may limit or enhance the treatment efficiencies.

Since electromigration is the movement of ionic contaminants in pore water toward electrodes under an electric field without convective movement, it is independent of the permeability of soils. Therefore, this phenomenon enables removal of contaminants from all types of soil. However, since electromigration affects only ionic species, it can only remove contaminants such as metal ions, dissolved organic acids and bases.

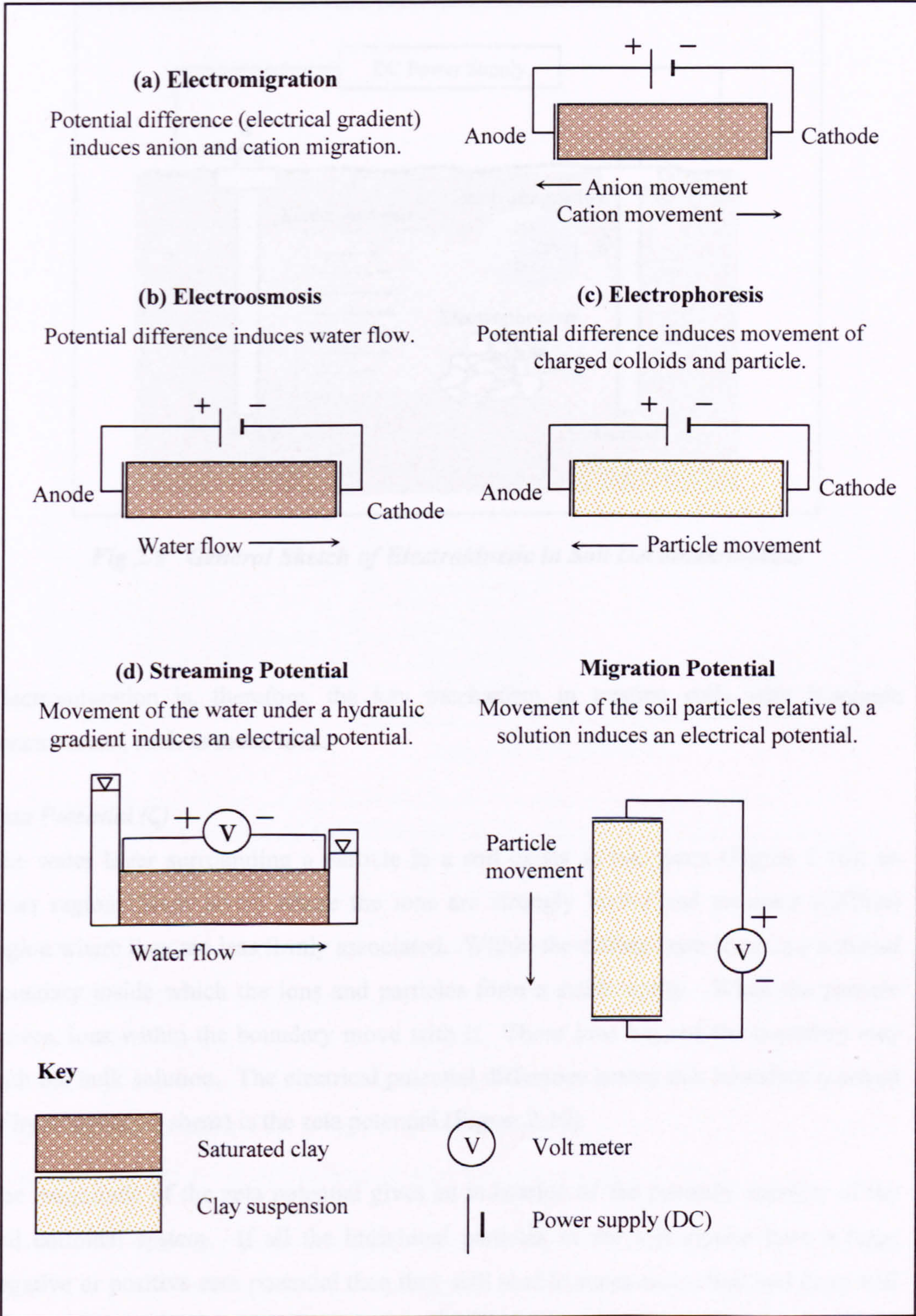


Fig 2.8 Electrokinetic Phenomena, (After Mitchell, 1991, 1993)

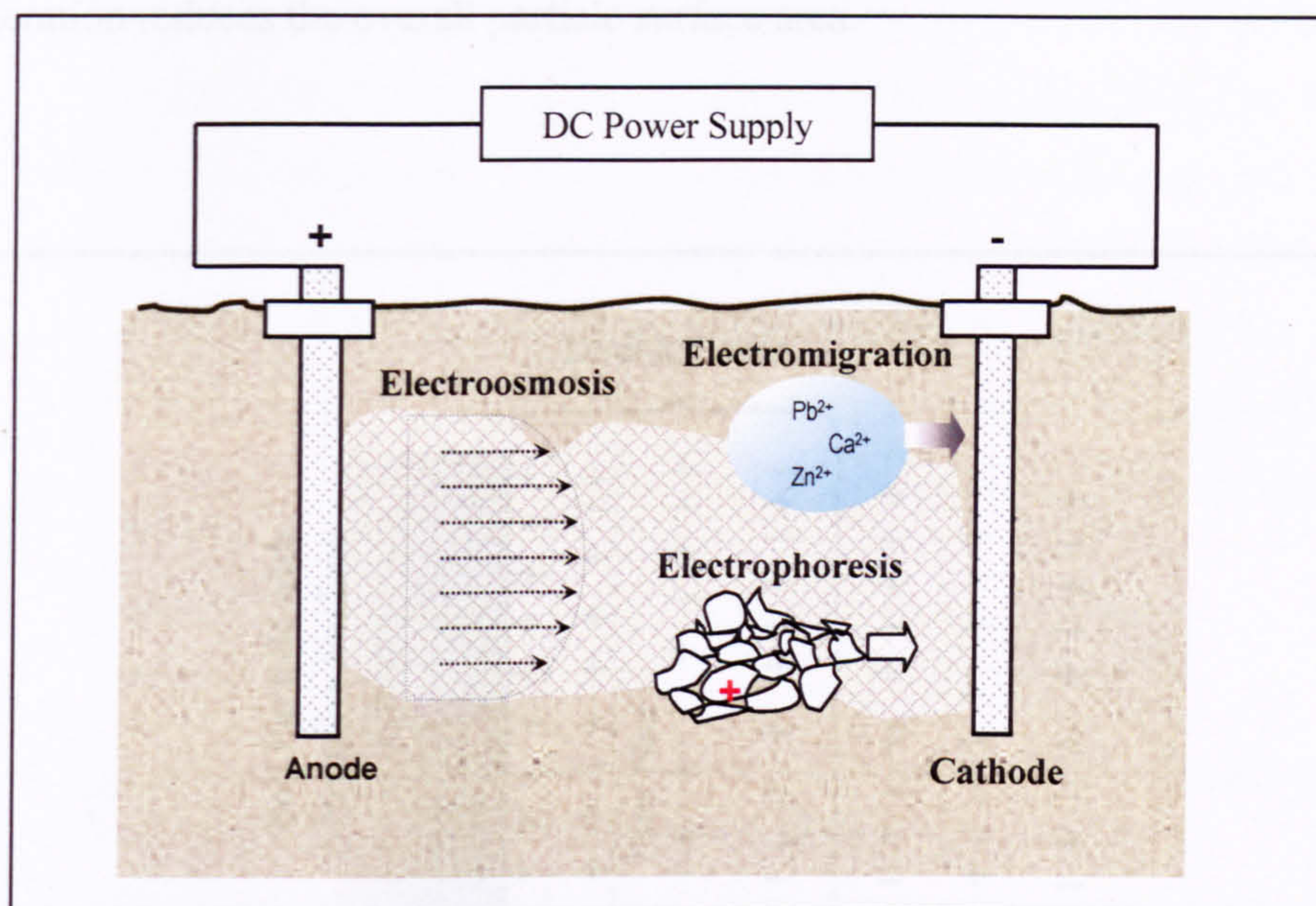


Fig 2.9 General Sketch of Electrokinetic in Soil Decontamination

Electromigration is, therefore, the key mechanism in treating soils with inorganic contaminants, such as metal ions.

Zeta Potential (ζ)

The water layer surrounding a particle in a soil exists as two parts (Figure 2.10); an inner region (Stern layer) where the ions are strongly bound and an outer (diffuse) region where they are less firmly associated. Within the diffuse layer there is a notional boundary inside which the ions and particles form a stable entity. When the particle moves, ions within the boundary move with it. Those ions beyond the boundary stay with the bulk solution. The electrical potential difference across this boundary (surface of hydrodynamic shear) is the zeta potential (Figure 2.10).

The magnitude of the zeta potential gives an indication of the potential stability of the soil colloidal system. If all the individual particles in the soil system have a large negative or positive zeta potential then they will tend to repel each other and there will be no tendency for the particles to come together. However, if the particles have low zeta potential values, the repulsive force will not be strong enough to overcome the Van

der Waals attraction between the particles, and they will begin to agglomerate. The agglomeration reduces the overall particle surface area.

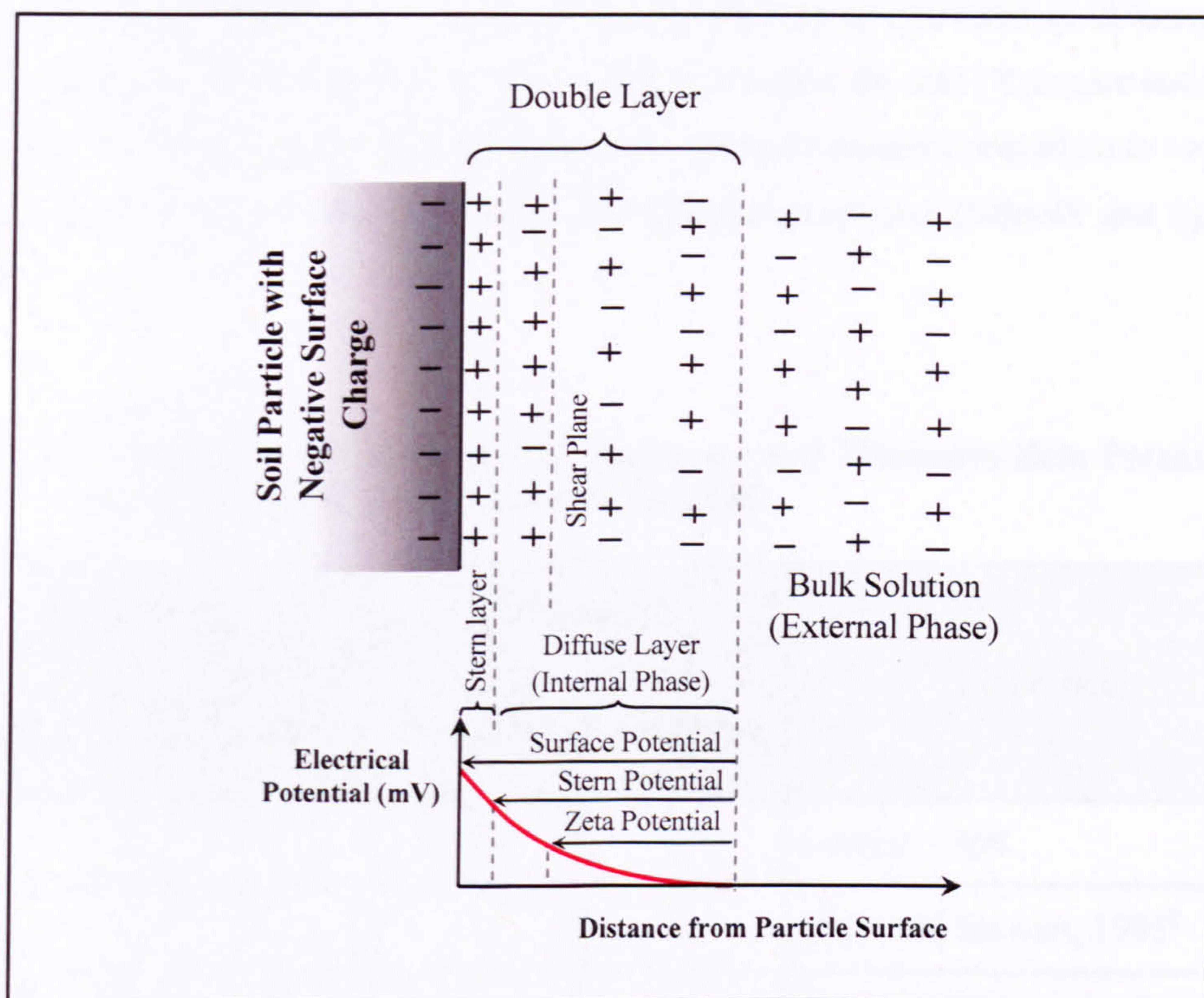


Fig 2.10 The Location of Zeta Potential on the Electrical Diffuse Double Layer

The most important factor that affects zeta potential is the pH. Soils, such as clays, have a negative surface charge once in water. As the environment pH increases by adding alkali, the soil particle surfaces become more negative, or at least less positive and the zeta potential will track this. If acid is added, ionisation causes the loss of hydroxyl ions which make the surfaces more positive. Consequently, the pattern is for the zeta potential to be more positive at low pH values and more negative at high pH values.

A number of investigators have studied variation of the zeta potential of kaolinite as a function of pH (refer to Table 2.3). Amongst them, there is general agreement that the zeta potential for kaolinite reduces in magnitude (becomes more positive) as acidity increases although significant variations may exist among published experimental data. The data in Table 2.3 is not intended to be comprehensive; rather to illustrate the ranges

of pH giving maximum and minimum zeta potential values as determined by different authors. The reported maximum magnitude is less than -55 mV in very basic solutions ($\text{pH} > 10$) with the exception of the data presented by Hotta et al. (1999) that reports the zeta potential as -65 and -85 mV. The differences between the authors are too large to be explained although some of the variations in the data may be attributed to differences in sample composition and preparation and models to interpret the data (Yukselen and Kaya, 2003). These diverse approaches are due to there being no standard procedure to treat and prepare the minerals to determine their electrokinetic properties (Schroth and Sposito, 1997).

Table 2.3 Comparison of the Reported Maximum and Minimum Zeta Potential of kaolinite (after Yukselen and Kaya, 2003)

Maximum		Minimum		Reference
pH	Zeta Potential (mV)	pH	Zeta Potential (mV)	
11	-40	3.5	≈ 7	Lorenz, 1969
12.3	-32	3	≈ 0	West and Stewart, 1995 ^b
10	-54	2	0.7	Vane and Zang, 1997 ^{a,1}
10	-40	0	2.2	Smith and Narimatsu, 1993 ^c
11	-30	3.5	5.5	Williams and Willams, 1977 ^d
11	-85	3	≈ 8	Hotta <i>et al.</i> , 1999 ^{a,1}
9.5	-65	3	≈ -3	Hotta <i>et al.</i> , 1999 ^a
12	-40	2	10	Dzenitis, 1997
7 and 11	-25	3	-8	Stephan and Chase, 2001 ^{a,1,2}
11	-43	3	-25	Stephan and Chase, 2001 ^{a,3}

^a Georgia kaolinite.
^b Speswhite kaolinite.
^c Lewiston, Montana.
^d Na kaolinite.
¹ With 0.01 M KCl,
² Low salt concentration.
³ 0.14 M NaCl.

Studies by Yukselen and Kaya, (2003) also found the zeta potential of kaolinite to be sensitive to the valence of ions. Their work revealed that the zeta potential of kaolinite decreased with divalent cations such as Ca^{2+} and Mg^{2+} . The zeta potential of kaolinite with heavy metal ions such as Cu^{2+} , Co^{2+} and Pb^{2+} showed a similar trend, i.e., increase in the concentration of these ions caused a decrease in the zeta potential up to neutral pH, then it became positive.

According to the Gouy-Chapman model, the thickness of diffuse double layer, $(1/K)$ is given by:

$$\frac{1}{K} = \left(\frac{E_0 D k T}{2 n_0 e^2 v^2} \right)^{1/2} \quad 2.3$$

Where:

E_0 = Permittivity of vacuum ($8.8542 \times 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1}$)

D = Dielectric constant of fluid medium (Water = 80 at 20°C)

k = Boltzmann Constant ($1.38 \times 10^{-23} \text{ J}^\circ\text{K}^{-1}$)

T = Temperature ($^\circ\text{K}$)

n_0 = Electrolyte concentration

e = Electronic charge ($1.602 \times 10^{-19} \text{ C}$)

v = Cation valence

Equation 2.3 reads that as the concentration of ions or the valency of ions increases, the thickness of the diffuse electrical double layer decreases resulting in a lower zeta potential.

In highly basic environments, the zeta potential became negative again, giving two apparent points of zero charge (surface carrying no net fixed charge). One of two apparent points of zero charges was attributed to kaolinite and the other one to the precipitation of these ions in highly basic solutions ($\text{pH} > 9$), (Yukselen and Kaya, (2003).

Cation Exchange Capacity

Cation exchange is the interchange between a cation (positively charged element) in a solution and another cation on the surface of any surface active material (Foth 1984). Cation-exchange capacity (CEC) is defined as the degree to which a soil can adsorb and

exchange cations. The cations are held on "exchange sites" (called miscelles) where one cation can be exchanged for the same type or a different cation. The higher the CEC, the higher the total negative charge of the soil, and the more cations that can be held. The CEC is expressed in milliequivalents per 100 grams (meq/100g) of soil.

Cations are exchanged in order of efficiency. Efficiency is dictated by two controlling variables; valence and hydrated radius. Hydrated ions with smaller radii will move closer to the miscellar surface and become more strongly adsorbed. Cations with a greater valence are absorbed more strongly than cations of a lower valence (Foth 1984). For example, below is a sequence of ions positioned in order of cation exchange efficiency;



A clay soil will have a larger CEC than a sandy soil. This is because smaller particles have a higher surface area to volume ratio. Gray (1966) performed tests proving that low activity clays with low CEC such as kaolin (refer to Table 2.4) are more electroosmotically efficient (i.e. transport more water per amp passed) than high activity clays with high CEC. Kaolin has little cation exchange capacity, because there is little if any isomorphous substitution (Foth, 1984), which is the mechanism by which clays obtain their characteristic net negative charge.

Soil pH is also important for CEC because as pH increases (becomes less acid), the number of negative charges on the colloids increase, thereby increasing CEC. This is illustrated by the three selected soil materials in Figure 2.11.

Table 2.4 Cation Exchange Capacity of Clay Minerals (After Foth, 1984)

Clay	CEC (me/100g)
Vermiculite	150
Montmorillonite (smectite)	100
Illite	25
Muscovite	5 - 20
Kaolin	3

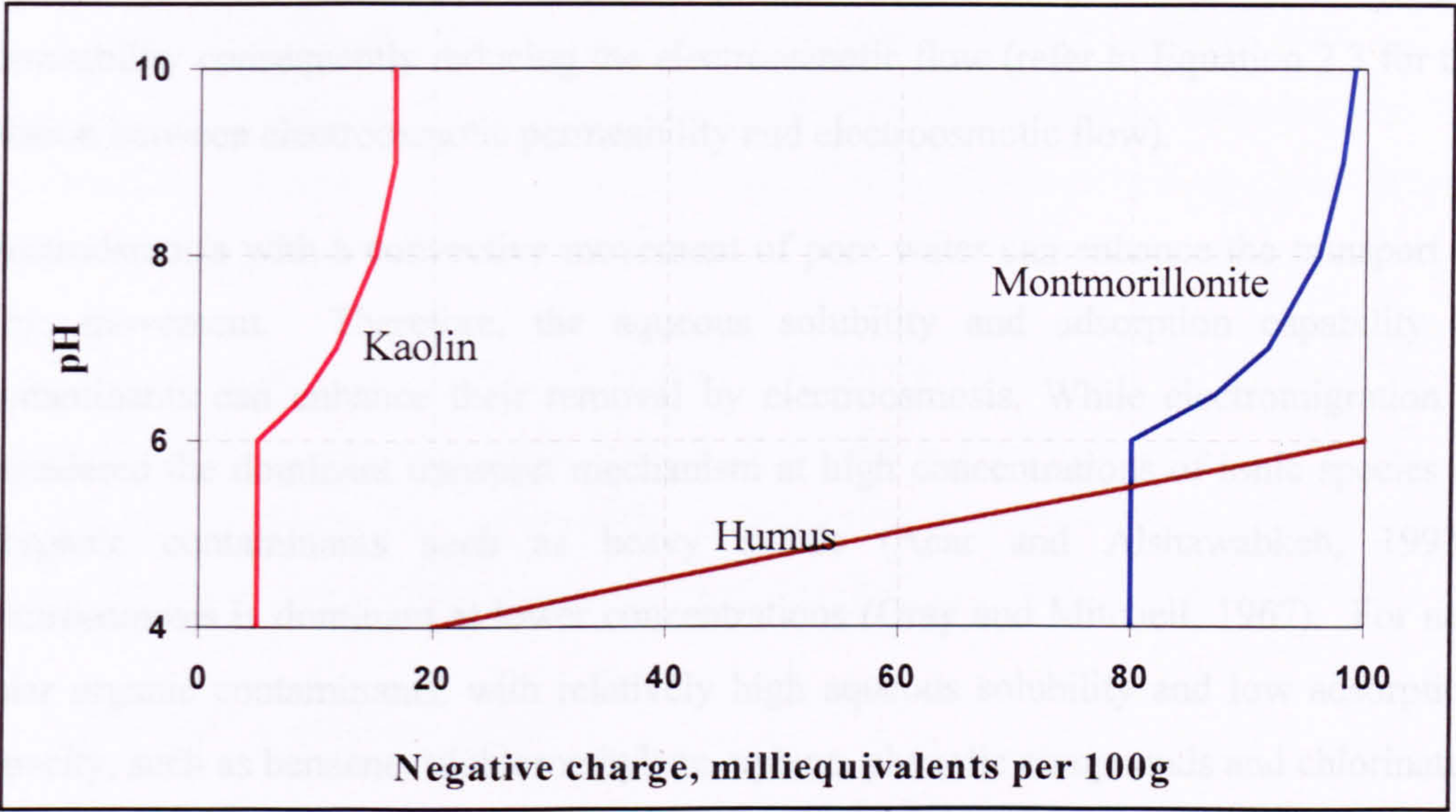


Figure 2.11 Relationship of CEC to pH (After Foth 1984)

Buffer Capacity

Cations on the exchange sites serve as a source of re-supply for those in the pore water which have electro migrated due to electrokinetic processes. The higher the CEC, the more cations that can be supplied. This is called the buffer capacity of the soil.

2.3.2.3 Electroosmosis

Electroosmosis is the movement of the pore fluid which contains dissolved ionic and non-ionic species, relative to the stationary soil mass, toward the cathode as a result of the application of a low direct current/voltage gradient to the electrodes (Pamukcu and Whittle, 1992; Shapiro and Probst, 1993) – Figure 2.8b.

Electroosmosis occurs because the surface of soil particles generally carry a negative charge. These charged surfaces attract positive ions in the pore water, which form a double layer (Figure 2.10). The electric field causes migration of the outer, mobile part of the double layer towards the cathode. Water in the pores between particles is drawn along by viscous drag. Since zeta potential controls the effective charge on the mechanical 'surface' of particles (refer to Section 2.3.2.1), changes in it will have a direct effect on the

rate of electroosmotic flow. For instance, studies by West and Stewart (1995) showed that when zeta potential became more positive and it reduced the electroosmotic permeability consequently reducing the electroosmotic flow (refer to Equation 2.3 for the relation between electroosmotic permeability and electroosmotic flow).

Electroosmosis with a convective movement of pore water can enhance the transport of ionic movement. Therefore, the aqueous solubility and adsorption capability of contaminants can enhance their removal by electroosmosis. While electromigration is considered the dominant transport mechanism at high concentrations of ionic species of inorganic contaminants such as heavy metals (Acar and Alshawabkeh, 1993), electroosmosis is dominant at lower concentrations (Gray and Mitchell, 1967). For non polar organic contaminants, with relatively high aqueous solubility and low adsorption capacity, such as benzene, trichloroethylene, xylene, phenolic compounds and chlorinated solvents, electroosmosis is considered to be the dominant process in electrokinetic remediation (Acar et al., 1992; Bruell et al., 1992; Pamucku and Wittle, 1993).

2.3.2.4 Electrophoresis

Electrophoresis is the transport of charged colloids and particles due to the application of a low direct current or voltage gradient relative to the stationary pore fluid, (Acar and Alshawabkeh, 1993) – Figure 2.8c. Colloids are made up of ionisable groups attached to large organic molecules, macromolecules, and aggregates of ions. Electrophoresis is dominant in remediating slurries or if surfactants are present in pore fluid, (Acar and Alshawabkeh, 1993). However, in compact systems such as glacial till, it is insignificant because the solid particles are not free to move (Pamucku and Whittle, 1992; Probstein and Hicks, 1993). In some cases, also, electrophoresis of clay particles may play a role in decontamination if the migrating particles have chemical species adsorbed on them.

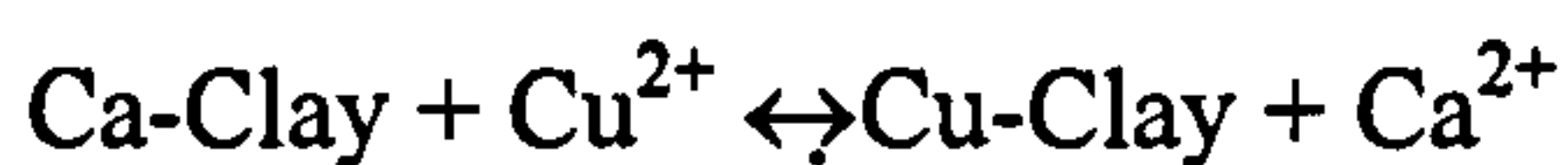
2.3.2.5 Auxiliary reactions

The mass flux transported during the electrokinetic process also depends on the transient geochemistry that takes place under the influence of an induced electrical field. Specifically, the sorption–desorption, precipitation–dissolution, and oxidation–reduction behaviour of the contaminants during the electrokinetic process significantly affect the remediation efficiencies, (Reddy and Shirani, 1997).

(a) Sorption and Desorption

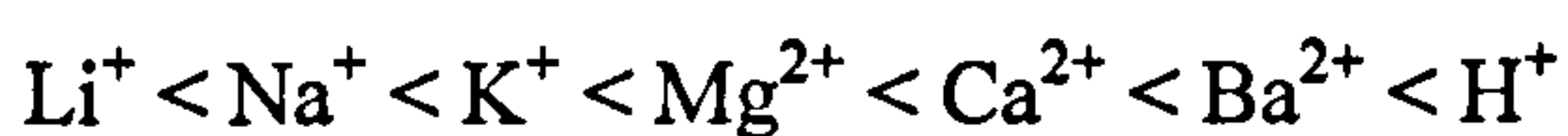
Sorption refers to the partitioning of the contaminants from the solution or pore fluid to the solid phase or soil surface. Sorption includes adsorption and ion exchange and it is dependent on the type of contaminant, the type of soil, and the pore fluid characteristics (Reddy and Shirani, 1997).

Most adsorption and ion exchange is caused by electrical charges on the surface or in the lattices of colloidal particles. Cations enter the interlayer exchange sites in clay only by exchanging a cation already in the interlay sites in order to maintain an electrically neutral state of the entire clay particle. Exchange of ions is observed as the following pattern:



Where Ca-Clay indicates the clay in the exchanging sites.

The amounts of various ions held in the exchange site are dependent on the ion exchange capacity. An observed sequence of replacing power of the common cations on clay is as follows:



In general, ions of greater charge are more strongly held in exchange sites with an exception of H^+ ions (Kim, 1998).

The replacing power of cations varies with the type of ion, it's size and degree of hydration, valence and concentration and the kind of clay mineral involved. As it is controlled by number of factors no single order of replacement can be given. All other factors being equal the replacing power of monovalent cations increases in the following order: $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{H}$ and for divalent cations: $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$. In case of mixture of monovalent and divalent cations as they exist in normal soils the replacing power increases in the following order: $\text{Na} < \text{K} < \text{NH}_4 < \text{Mg} < \text{Ca} < \text{H}$. This means Na is more easily replaced than K and K more easily than NH_4 and so on.

In electrostatic cation exchange, smaller cations with higher valence (charge per atom) are held more tightly to exchanges sites than are larger cations with lower valence.

Desorption is the reverse process and is responsible for the release of contaminants from the soil surface, (Reddy and Shirani, 1997). Both sorption and desorption are affected by soil pH changes caused by the migration of H^+ and OH^- ions, which are produced by the electrolysis reactions (Acar and Alshawabkeh, 1993). The pH value at which they are affected varies from metal to metal under particular conditions (Evanko and Dzombak, 1997). In Figure 2.12, for example, the extent of sorption of several metal cations onto kaolin is shown as a function of pH for a particular background electrolyte composition. It may be seen there that the percentage sorption of metal cations onto kaolin generally increases with pH. It is also noted that copper sorbs extensively at much lower pH values than zinc or cadmium (Spark et al., 1997).

Generally, in acid conditions, adsorption is a more important process than the precipitation of solid phases in decreasing the concentration of metal ions in solution and the reverse is true in alkaline conditions (Elliott et al., 1986; Yong et al., 1993).

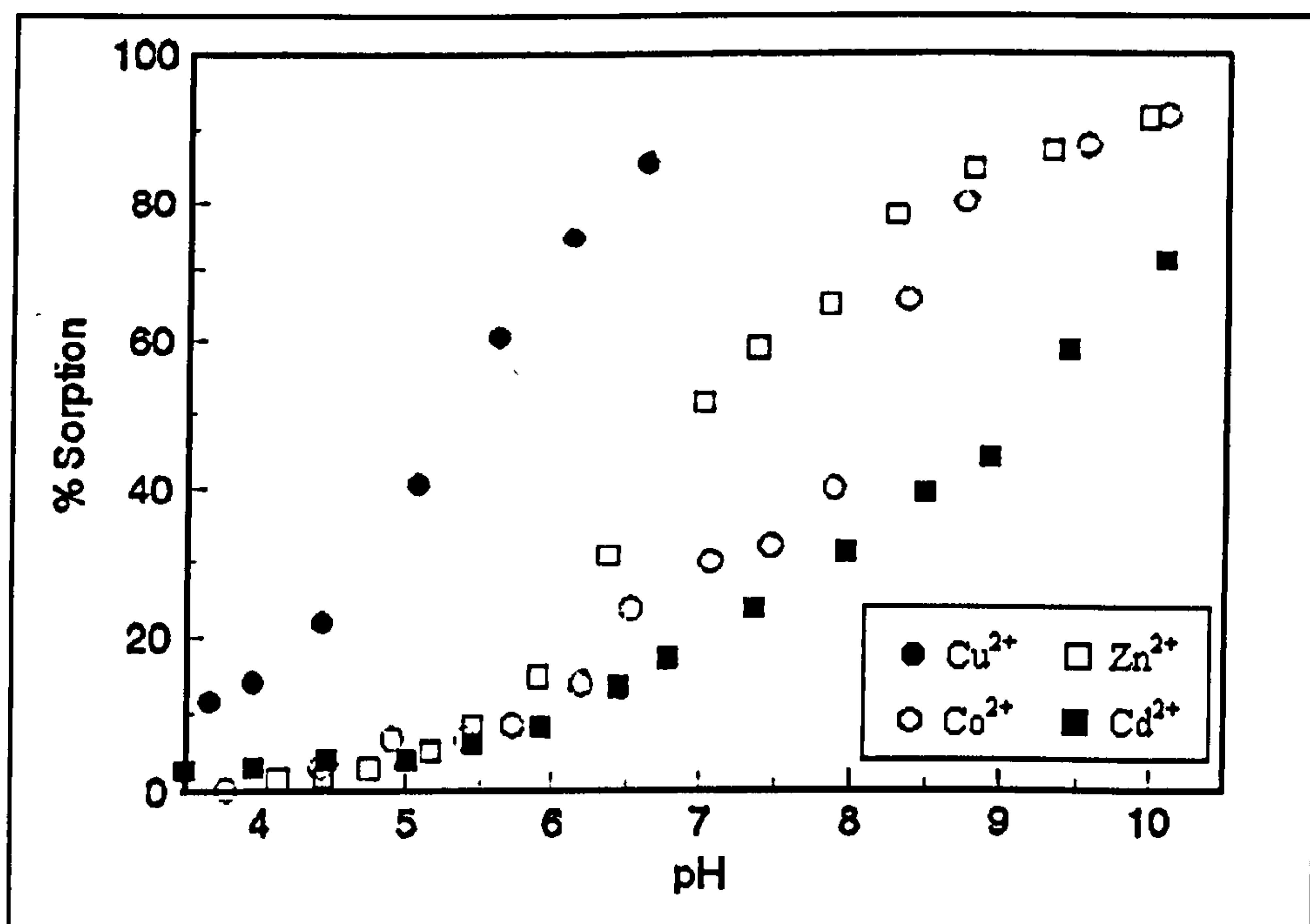


Fig 2.12 Metal Adsorption to Kaolin (in a Kaolin - Acid system with 0.1M NaCl) - After Spark et al., 1997

(b) Precipitation and Dissolution

Precipitation refers to the formation of solids from a solution during a chemical reaction. Dissolution occurs when a substance dissolves into a solution.

The precipitation and dissolution of the contaminant species during the electrokinetic process can significantly influence the removal efficiency of the process (Acar and Alshawabkeh, 1993). The soil decontamination process is affected by the H^+ ions generated at the anode migrating across the contaminated soil and neutralizing the OH^- ions at the cathode. However, in some types of soils, the migration of the H^+ ions will be hindered due to the relatively high buffering capacity of the soil. The presence of the OH^- ions at the cathode will increase the pH value ($pH = 10-12$). In a high pH environment, heavy metals will precipitate, and come out of solution. The precipitates consequently impede the movement of contaminants and water under an electric field. Figure 2.13 below shows a typical example of an unenhanced process which results in the precipitation of copper hydroxide.

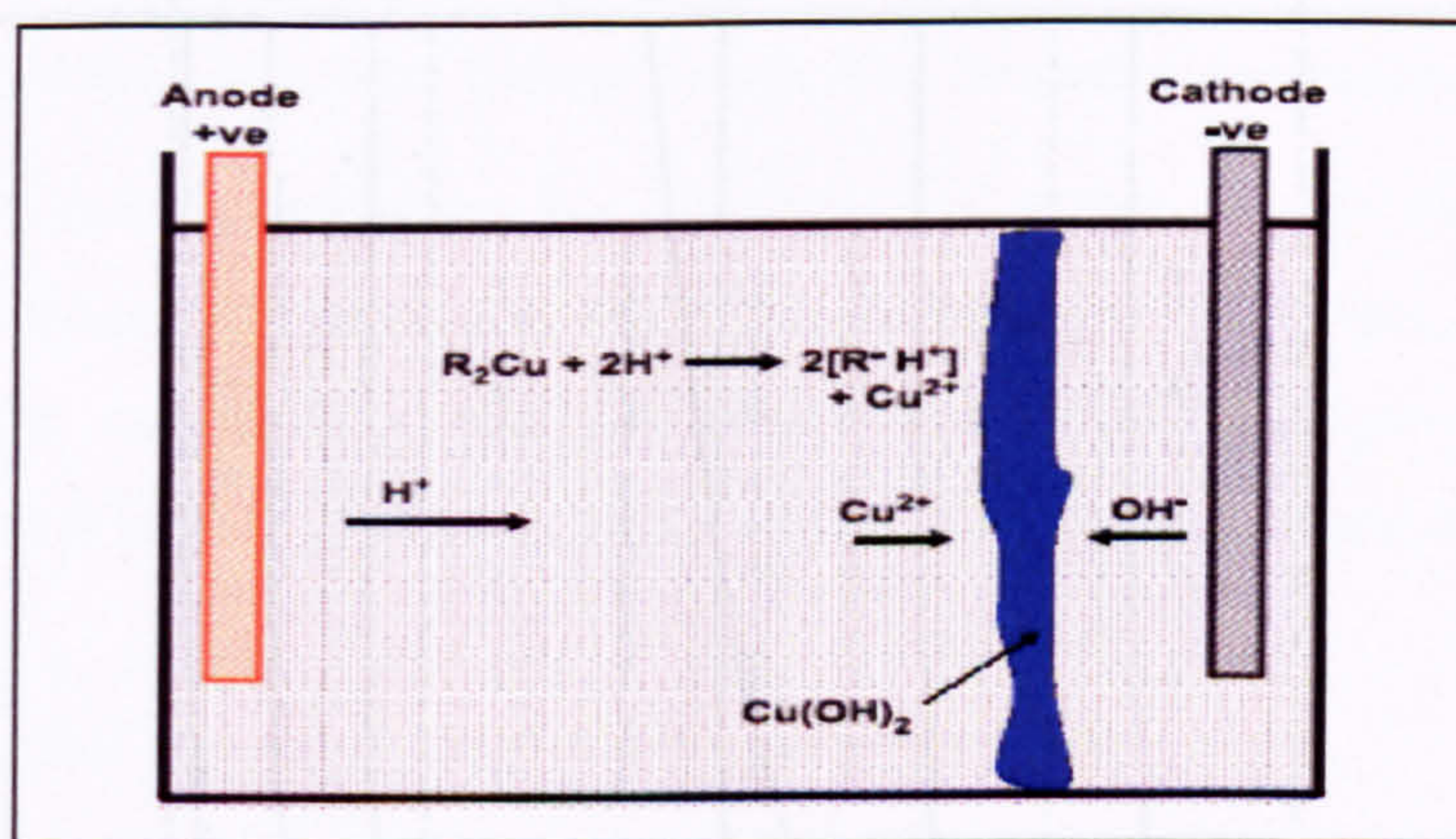


Fig 2.13 Unmanaged Electromigration of Copper Ions in a Typical Top soil, Resulting in Precipitation of $Cu(OH)_2$, (After Lageman et al., 2004)

The high pH and low heavy metals concentration condition at the cathode may also lead to the formation of a negatively charged complex species at the cathode compartment. The movement of these negatively charged complex species towards the anode and of the heavy metals towards the cathode relies upon relative mobility of H^+ ions. In other words, species migration ceases at a region closer to the cathode where the pH varies substantially because this is most likely to be where heavy metals accumulate and

eventually precipitate, clogging soil pores and hindering the remediation process, (Reddy and Shirani, 1997).

According to various researchers (Chuan et al., 1996; Thornton, 1996), metal solubility tends to increase at lower pH and decrease at higher pH values. This point is also demonstrated in Figure 2.14. The figure illustrates the significant decrease in the solubility (of each cationic metal compound) with increasing pH. For efficient metal contaminant removal, it is essential to have the contaminants in dissolved form during the electrokinetic process. Therefore it is important to control the pH by maximizing the spread of the acidic front generated from the anode so as to prevent precipitation.

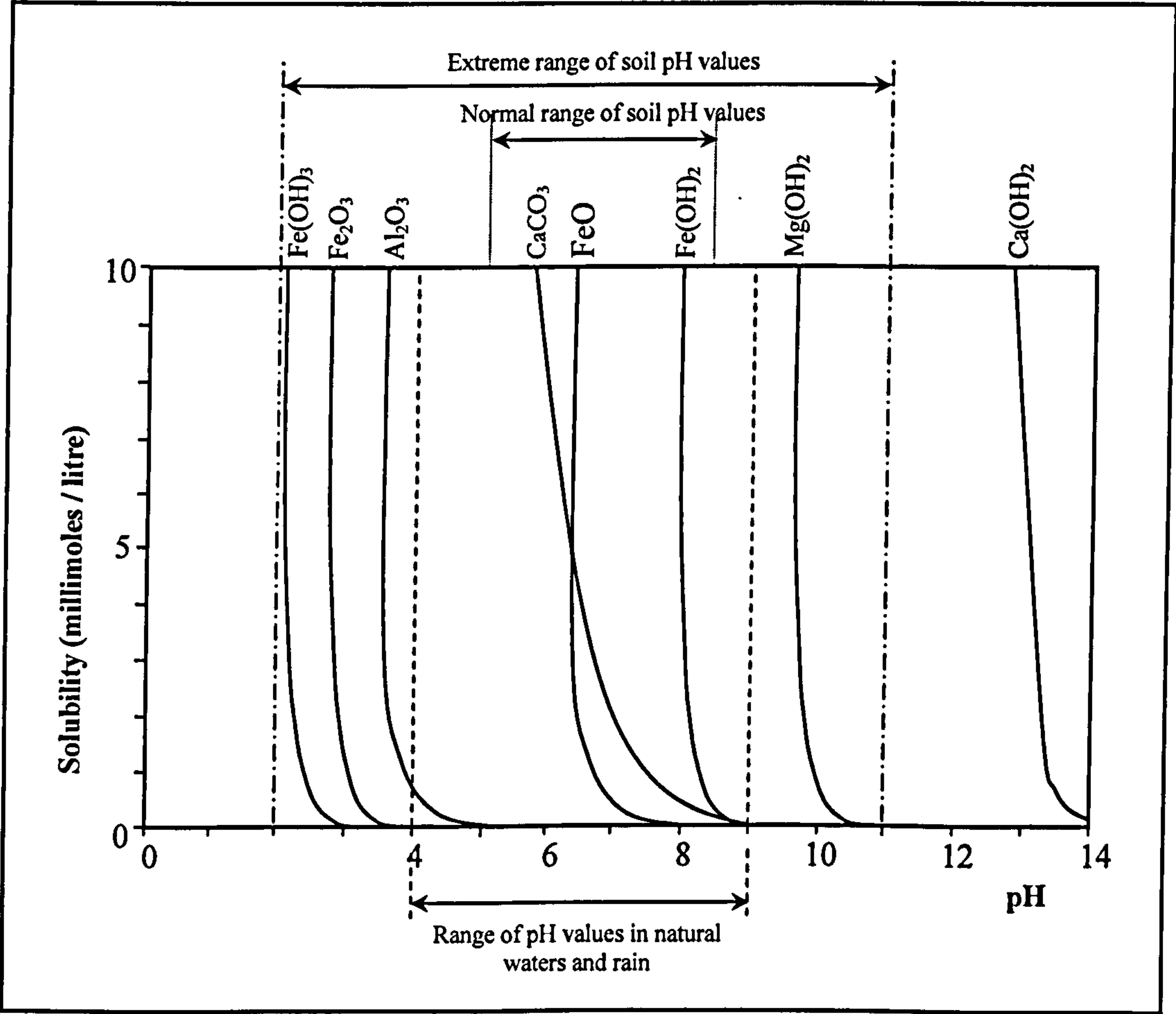


Fig 2.14 Solubility of Some Soil Mineral Species in Relation to pH, (After Loughnan, 1969)

(c) Oxidation–Reduction

Oxidation and reduction reactions are important when dealing with metallic contaminants such as chromium (Reddy and Shirani 1997). Chromium exists most commonly in two valence states: trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI). Cr(III) exists in the form of cationic hydroxides such as $\text{Cr}(\text{OH})^{2+}$ and it will migrate towards the cathode during electrokinetic remediation. However, Cr(VI) exists in the form of oxyanions such as CrO_4^{2-} , which migrate towards the anode. The valence state depends on the soil composition, especially the presence of reducing agents such as organic matter and Fe(II) and/or oxidizing agents such as Mn(IV), so it is important to know the valence state of metals and their possible redox chemistry.

(d) Diffusion

Diffusion refers to the ionic and molecular constituent forms of the contaminants moving from areas of higher concentration to areas of lower concentration because of the concentration gradient or chemical kinetic activity, and during electrokinetic remediation is thought to be insignificant (Shackelford and Daniel, 1991).

2.3.3 Factors that Affect the Electrokinetic Soil Remediation Technique

A number of factors determine the direction and extent of the migration of the contaminant. Such factors include: the type and structure of the soil, applied current density, sample conditioning and the electrode material, (Lindgren et al., 1992; Alshawabkeh et al 1999). This section aims at discussing these four factors in detail.

2.3.3.1 Soil Type and Physical Properties

According to Acar (1992), there should not be any technical restriction on the type of soil to be cleaned. However, metal contaminant mobility and transport efficiencies depend heavily on the physical properties of the soil and environmental variables (Alshawabkeh et al 1999). Soils with fine particles ($<100 \mu\text{m}$) are more reactive and have a higher specific surface area than coarser material (Evanko and Dzombak, 1997). As a result, the fine fraction of a soil often contains the majority of the contamination. The distribution of particle sizes with which a metal contaminant is associated can therefore determine the effectiveness of the technology (Dzombak et al., 1994).

Soil water influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depends on the soil water content. Soils of high water content, high degree of saturation, and low activity provide the most favourable conditions for transport of contaminants by electroosmotic advection and ionic migration. However, soils of high activity, such as illite, montmorillonite, and impure kaolinite, exhibit high acid/base buffer capacity and require excessive acid and/or enhancement agents to desorb and solubilise contaminants sorbed on the soil particle surface before they can be transported through the subsurface and be removed (Yeung et al. 1996, 1997; Puppala et al. 1997).

The technology can be applied to treat heterogeneous soil deposits effectively (Alshawabkeh et al 1999). For practical purposes, electroosmotic fluid volume flow rate is described by an equation analogous to Darcy's law;

$$Q = k_e i_e A \quad 2.3$$

where:

Q = fluid volume flow rate (m^3/s);

k_e = coefficient of electroosmotic permeability ($\text{m}^2/\text{V-s}$);

$i_e = \nabla(-\phi)$ = electric field strength (V/m);

ϕ = electric potential applied (V); and

A = total cross-sectional area perpendicular to the direction of fluid flow (m^2).

Values of hydraulic permeability for different types of soils can vary by many orders of magnitude (Freeze and Cherry 1979). For a contaminated soil deposit containing interlayers of fine sand and clay, typical values of hydraulic permeability of these strata are 1×10^{-4} and 1×10^{-9} cm/s, respectively (Mitchell 1993). However, values of the coefficient of electroosmotic permeability of different soils lie in the narrow range of 1×10^{-5} to 1×10^{-4} $\text{cm}^2/\text{V-s}$ (Acar and Alshawabkeh 1993; Mitchell 1993; Yeung 1994). Therefore, an electric field is a much more effective force in driving fluid through fine-grained soils of low hydraulic permeability than a hydraulic gradient and vice versa for coarse-grained soils of high hydraulic permeability.

As a result, the electric field strengths in the different soil layers will be similar when an externally electric potential is applied across the deposit. As the coefficient of electroosmotic permeability is generally insensitive to soil type, the electroosmotic fluid volume flow rates in different soil layers will thus be about similar as indicated by Equation 2.3. As a result, similar electroosmotic advection rates of contaminant transport can be generated in different soil layers within the heterogeneous deposit resulting in a more homogeneous cleanup.

2.3.3.2 Voltage and Current Levels

The electric current intensities used in most studies are of the order of a few tens of milliamperes per square centimetre. Although a high current intensity can generate more acid and increase the rate of transport to facilitate the contaminant removal process, it increases power consumption tremendously as power consumption is proportional to the square of electric current. An electric current density in the range of 1–10 A/m² has been demonstrated to be the most efficient for the process (Alshawabkeh et al 1999). However, appropriate selection of electric current density and electric field strength depends on the electrochemical properties of the soil to be treated, in particular the electric conductivity. The higher the electric conductivity of the soil is, the higher the required electric current density will need to maintain the electric field strength required. An optimum electric current density or electric field strength should be selected based on soil properties, electrode spacing, and time requirements of the process (Alshawabkeh et al 1999).

2.3.3.3 Enhancement

In some cases, an acid front may not be able to develop by electrokinetic processes because of the high acid/base buffer capacity of the soil and/or reverse electroosmotic flow, i.e., from the cathode toward the anode (Yeung et al. 1996, 1997). Under these circumstances and in order to promote solubilization and transport of the metallic species, enhancement agents may be needed. In addition to the economic considerations, any enhancement agents selected for the process must satisfy the following criteria (Reddy et al, 1997; Yeung et al., 1997; Rodsand, et al., 2000; Virkutyte et al. 2002):

- a) they should prevent the precipitation and adsorption of contaminants within the range of pH values expected to develop during the process (Section 2.3.2.4),

- b) they should prevent any reaction with contaminants that may cause precipitation. Instead, they should form soluble complexes with the contaminant that can electro migrate efficiently under a DC electric field,
- c) they should be chemically stable over a wide range of pH values,
- d) they should have a higher affinity for the contaminant than the soil particle surface,
- e) they and the resulting complexes should not have a strong affinity for the soil particle surface,
- f) the resultant ionic conductivity across the specimen should not increase excessively in a short period of time to avoid a premature decrease in the electroosmotic transport,
- g) they should prevent the generation of waste products or toxic by-products as a result of electrochemical reactions,
- h) they should not induce excessive solubilization of soil minerals or increase the concentrations of any regulated species in the soil pore fluid

Different schemes have been proposed and evaluated to enhance transport and extraction of cationic species under a DC electric field and to prevent the formation of immobile precipitates. To neutralize the hydroxyl ions generated by electrolytic reduction of water, acids such as acetic acid, hydrochloric acid may be introduced at the cathode (Acar and Alshawabkeh 1993; Puppala et al. 1997). Chelating or complexing agents, such as citric acid and ethylenediamine tetraacetic acid (EDTA), have also been demonstrated to be feasible for the extraction of different types of metal contaminants from fine-grained soils (Pamukcu and Wittle 1992; Eykholt and Daniel 1994; Yeung et al. 1996; Wong et al. 1997).

The choice of enhancement agent, though, is contaminant specific (Alshawabkeh et al 1999). If the primary function of the enhancement agent is to desorb the contaminant from the soil particle surface, the sorption characteristics of the contaminant on the soil particle surface in the presence of the enhancement agent as a function of the value of pH must be carefully studied. This is because the presence of the enhancement agent can

change the sorption characteristics completely. For example, results obtained by Yeung et al. (1996) indicated that the addition of EDTA promoted sorption of lead and cadmium onto kaolinite particle surfaces in an acidic environment, rendering these metal contaminants immobile. The ability of the enhancement agent to form complexes with the metal contaminant may also be pH dependent. Therefore, although the formation of complexes in free solution can be predicted by solving simultaneous chemical equilibrium equations using appropriate equilibrium constants, the behaviour of these complexes in the presence of soil at different pH values should also be evaluated experimentally. The concentration of the enhancement agent required must also be carefully determined from these laboratory investigations.

2.3.3.4 Electrode Material and Spacing

To prevent dissolution of the electrode and generation of undesirable corrosion products during electrolysis, chemically inert and electrically conducting materials such as graphite, coated titanium, or platinum should be used (Virkutyte et al. 2002). Important considerations for the choice of electrode material are (Alshawabkeh et al 1999);

- a) electrical conduction properties of the material,
- b) availability of the material,
- c) ease of fabrication to the form required for the process,
- d) ease of installation in the field, and
- e) material, fabrication, and installation costs.

Regardless of the material selected for the electrode, the electrode has to be installed properly in the field so that it can make good electrical contact with the subsurface. Moreover, the design must make provisions to facilitate exchange of solution with the subsurface through the electrode.

When selecting spacing between electrodes, issues of costs and processing time need to be considered. Larger electrode spacing will reduce the number of boreholes and installation costs, but will increase the processing time required and operation costs.

2.3.4 Available Electrokinetic Soil Remediation Technologies

To overcome some of the limitations listed in Section 2.2.2.5, different electrolyte cells and remediation techniques have been proposed and tried in the electrokinetic remediation processes of heavy metals by researchers and commercial vendors in various applications. This subsection aims to describe these different electrokinetic remediation technologies currently under development for use at contaminated sites.

2.3.4.1 Cation-Selective Membrane Model

In order to deal with the pH impact so as to improve the overall remediation process, researchers (such as Li and Neretnieks, 1998; Li and Li 2000) proposed the use of a cation-selective membrane as an ion barrier (Figure 2.15). The membrane, placed between the soil and cathode, allows cations and very few anions to pass through it. Almost all the hydroxyl ions produced at the cathode remain on the cathodic side of the membrane. Meanwhile, the hydrogen ions generated at the anode move through the soil and into the membrane. The basic front cannot pass through the membrane, where it meets the acidic front, thereby maintaining a low pH in most of the soil. The cations that are small enough to go through the membrane will reach the cathode where they are targeted for removal.

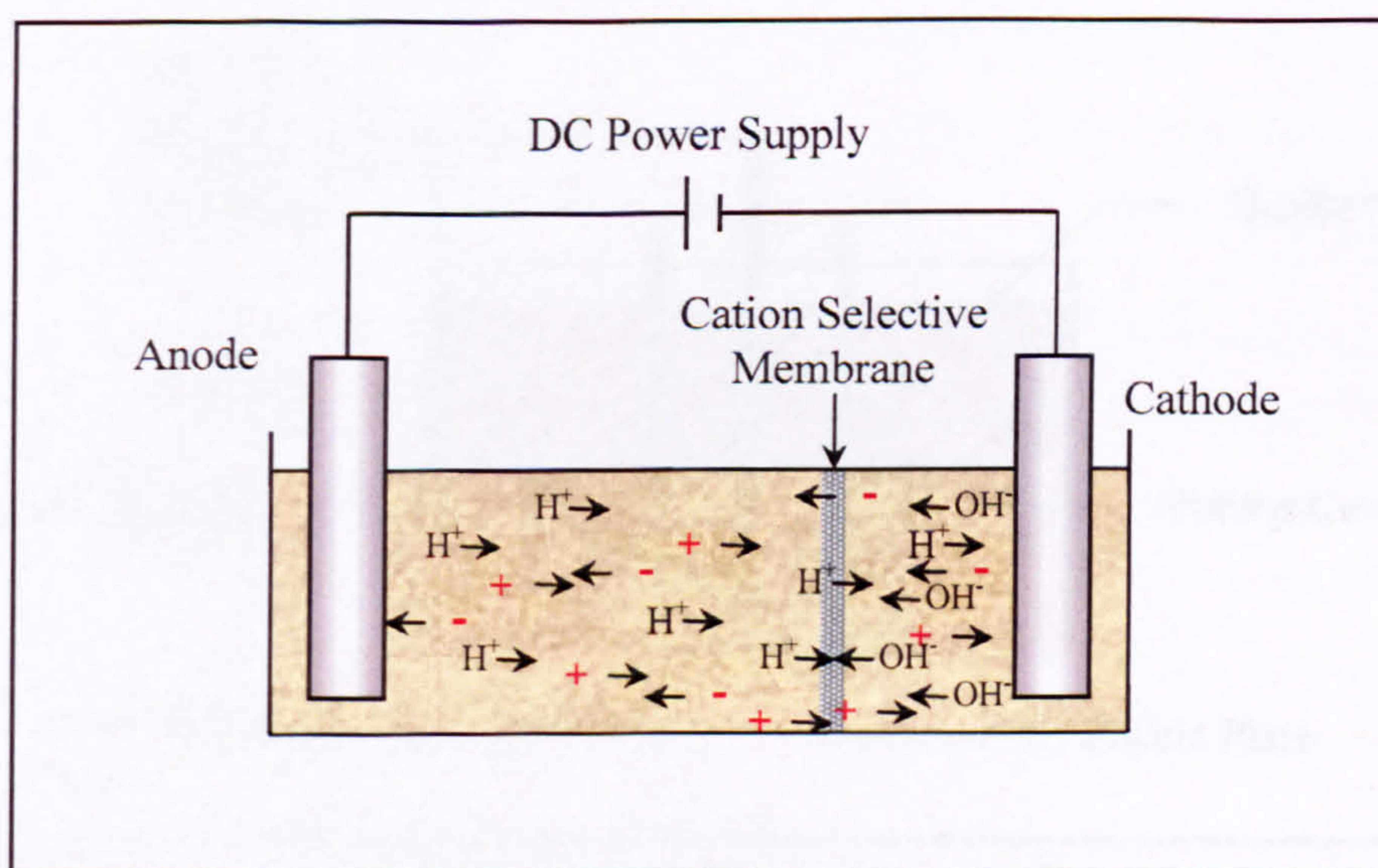


Fig 2.15 Cation Selective Membrane Process Sketch

2.3.4.2 *Surfactant-coated Ceramic Casings Model*

In order to control the hydraulic flux of water in the treated soil so that the water content at the anode does not become too low hampering soil conductivity during electrokinetic remediation, Mattson and Lindgren, (1995) proposed the use of porous ceramic castings. During the application, the direction of electroosmotic flow in porous ceramic media has a strong influence on the amount of water being added to the soil from the ceramic castings.

In this model, the cell consisted of; a plastic container filled with buffering solution, polyvinyl chloride plate glued to the bottom of the container, porous ceramic castings, woven wire cathode and graphite anode (Figure 2.16). The most suitable buffering solution for this experiment is a phosphate solution with a pH of 6 (Mattson and Lindgren, 1995). To overcome the hydraulic counter flow, the experiment should only be conducted until the fluid level difference between the inner and outer reservoirs becomes >1 cm (Mattson and Lindgren, 1994).

The use of anode ceramic casting may significantly improve the application of electrokinetic remediation in unsaturated soil. However, the technique would only be suitable for long-term remediation processes if it was ensured that electroosmotic flow occurred from the surrounding soil towards the interior of the anode casting.

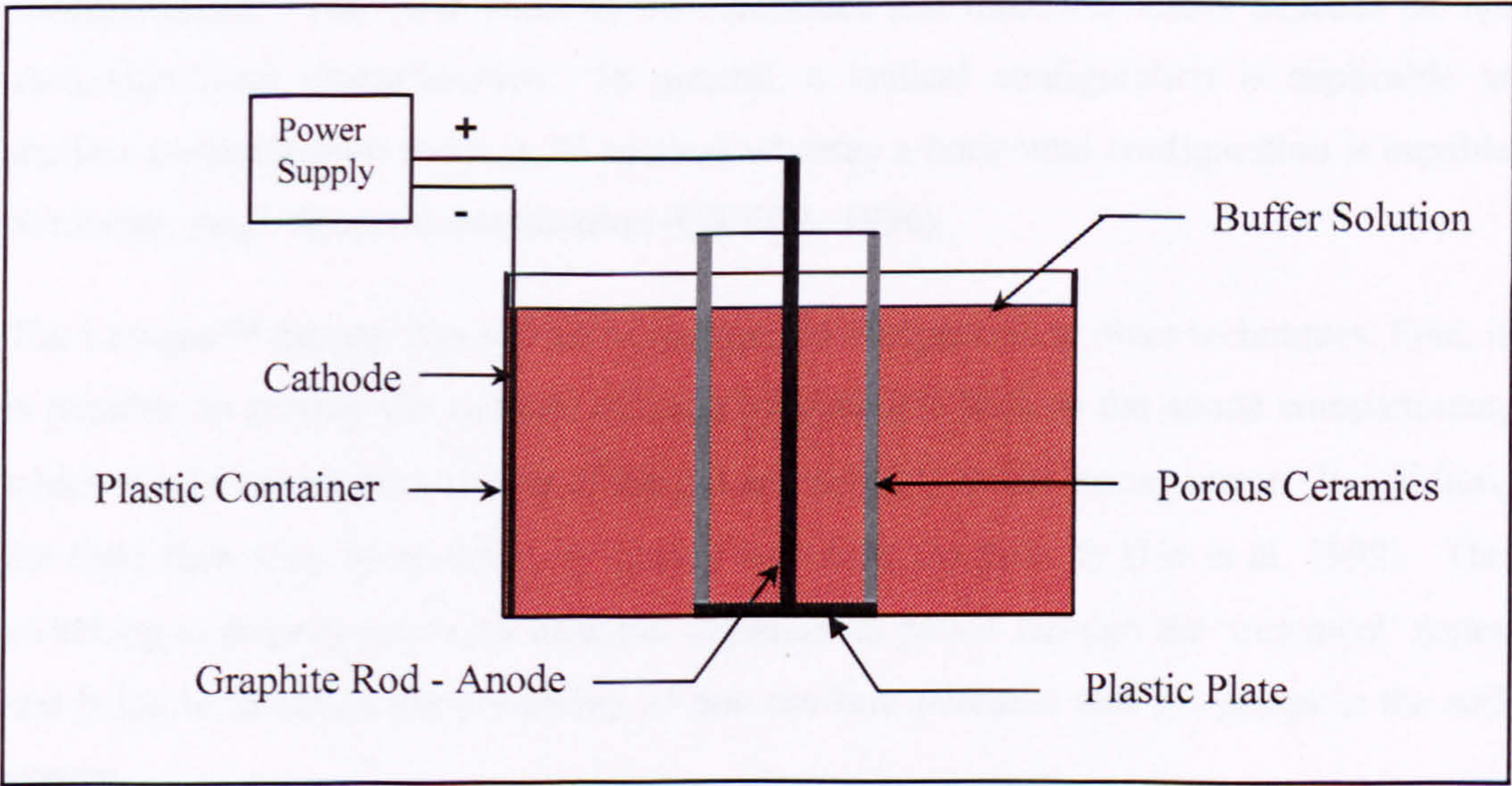


Fig 2.16 *Electrokinetic Cell with Ceramic Castings, (After Mattson and Lindgren, 1995)*

2.3.4.3 *Lasagna™ Model*

In 1995 a novel integrated method for in situ electrokinetic remediation of soils, called Lasagna™, was developed and implemented at the Paducah site, in Kentucky, USA. The original process concept involved using horizontal electrodes sandwiching treatment zones making it look like lasagna – hence where it derived its name. This technology is useful for removing heavy metal contaminants from heterogeneous, low-permeability soils (Ho et al., 1997; Ho et al., 1999).

Major features of the process are (US DOE, 1996):

- Electrodes energized by direct current, which cause water and soluble contaminants to move into or through the treatment layers and also heat the soil;
- Treatment zones containing reagents that decompose the soluble organic contaminants or adsorb contaminants for immobilization or subsequent removal and disposal; and
- A water management system that recycles the water that accumulates at the cathode (high pH) back to the anode (low pH) for acid-base neutralization. Alternatively, electrode polarity can be reversed periodically to reverse electroosmotic flow and neutralize pH.

Both horizontal (Figure 2.17) and vertical (Figure 2.18) configurations have been conceptualized. The orientation of the electrodes and treatment zones depends on the site/contaminant characteristics. In general, a vertical configuration is applicable to shallow contamination (within 15 metres) whereas a horizontal configuration is capable of treating much deeper contamination (US EPA, 1996).

The Lasagna™ process has several advantages in comparison to other techniques. First, it is possible to recycle the cathode effluent by aiming it back to the anode compartment, which would favour neutralising of the pH and simplify water management. In addition, the fluid flow may be reversed by simply switching the polarity (Ho et al. 1999). The switching of polarity promotes multiple contaminant passes through the ‘treatment’ zones and helps to diminish the possibility of non-uniform potential and pH jumps in the soil system.

According to laboratory experiments and promising pilot-scale studies at the Paducah site in Kentucky, Lasagna™ technology may become one of the most widely used electrokinetic remediation technologies for removing heavy metal contaminants from various soils. Nevertheless, there are several technological and other limitations, which should be improved for future studies. It is obvious that Lasagna™ technology is potentially capable of treating multiple contaminants in clay and laden soils, but additional experiments and studies should be conducted in order to assure that the treatment process is compatible for individual contaminants. In addition, one of the biggest technology drawbacks is the entrapment of gases formed by electrolysis and the assurance of good electrical contact to the electrodes (Virukyte et al., 2002).

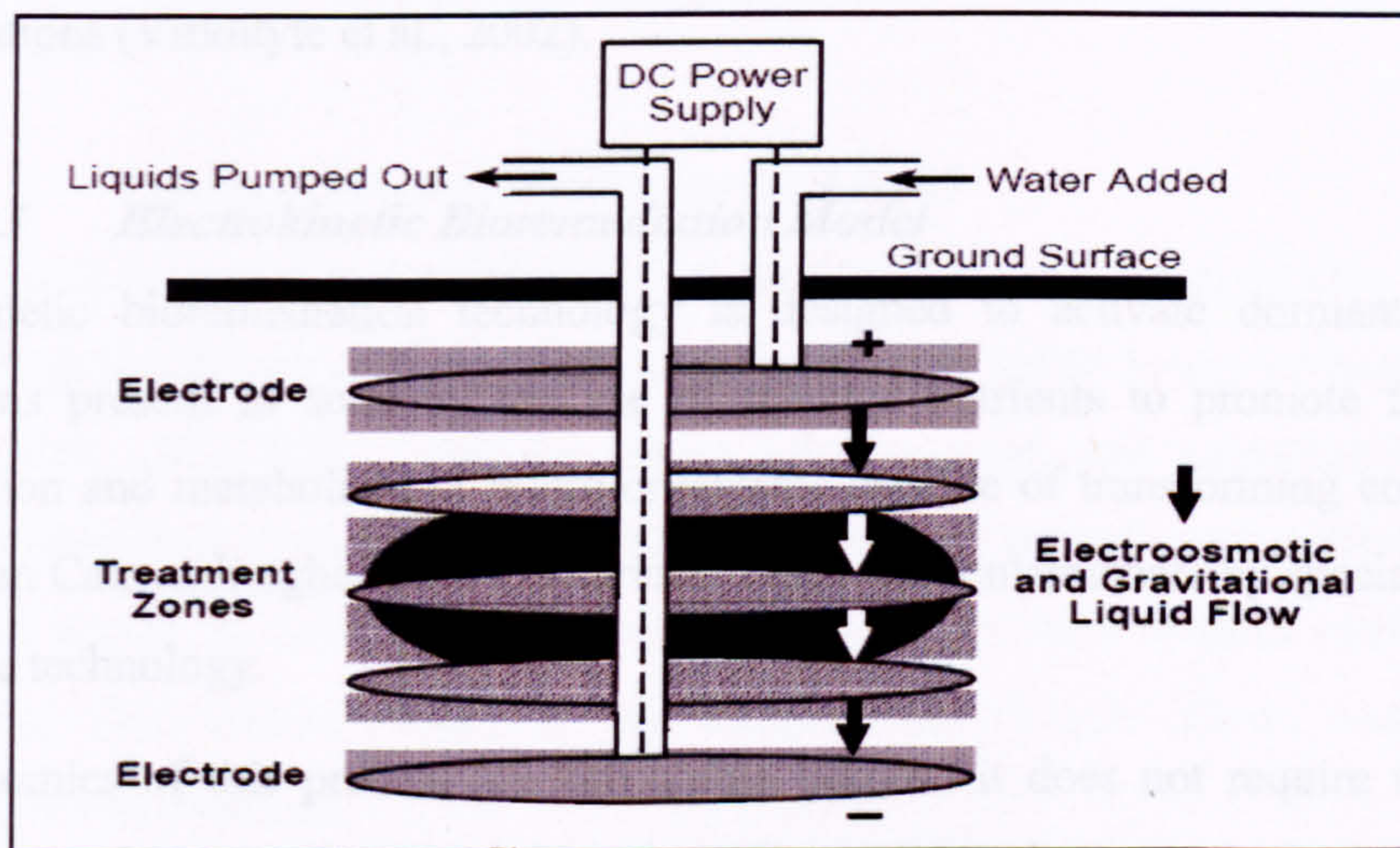


Fig 2.17 Horizontal Configuration Lasagna™ Cell, (After Roulier et al., 2002)

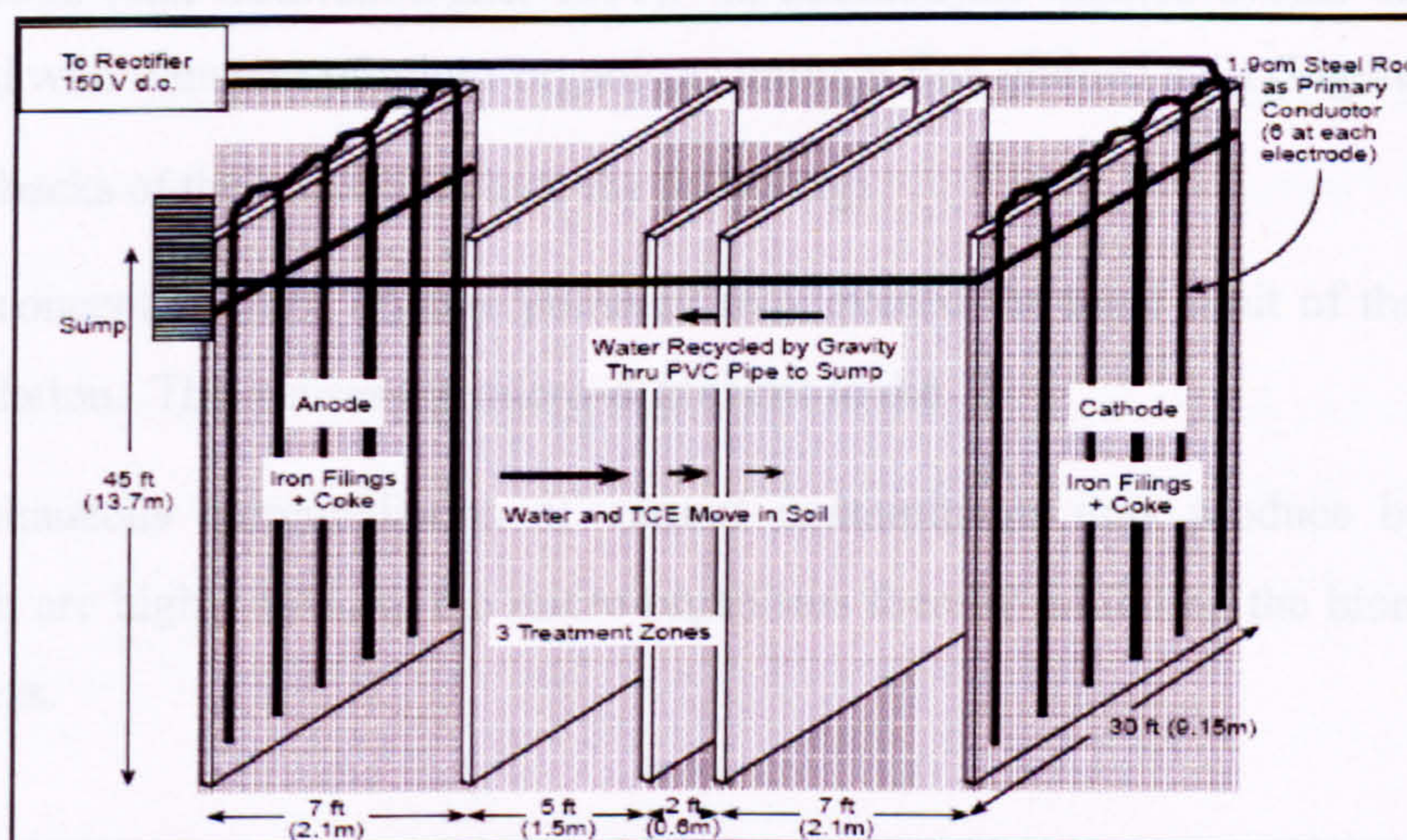


Fig 2.18 Lasagna™ Vertical Configuration, (After Roulier et al., 2002)

2.3.4.4 *Electro-Klean™ Electrical Separation Model*

Electro-Klean™ technology was applied in-situ, as well as ex-situ, in Louisiana, USA. It is a process that removes or captures heavy metals, radionuclides, and selected volatile organic pollutants from saturated or unsaturated sands, silts, fine-grained clays, and sediments. In its application, electrodes are placed on each side of the contaminated soil mass, and direct current is applied. In order to improve the remediation efficiency, conditioning fluids (mostly acids) are added or circulated at the electrodes to enhance the electrochemistry of the process. The concurrent mobility of the ions and pore fluid decontaminates the soil mass. Contaminants are electroplated on the electrodes or separated in a post-treatment unit (US EPA, 1995). The main limitations of this technique are the high buffering capacity of the soils and different coexisting chemicals and their concentrations (Virkutyte et al., 2002).

2.3.4.5 *Electrokinetic Bioremediation Model*

Electrokinetic bioremediation technology is designed to activate dormant microbial populations present in soils by the use of selected nutrients to promote the growth, reproduction and metabolism of micro-organisms capable of transforming contaminants in soil (van Cauwenberghe, 1997). Nutrients reach the contaminants by specially applied bioelectric technology.

The economics of this process are favourable because it does not require an external microbial population to be added into the soil system and nutrients can be uniformly dispersed over the contaminated soil or directed to a specific location, thus reducing nutrient costs (van Cauwenberghe, 1997). In addition the method avoids the problems associated with transport of micro-organisms through fine-grained soils (Figure 2.19).

The drawbacks of the process include the following;

- The concentration of organic pollutant may exceed the toxic limit of the microbial population. This causes the micro-organisms to die.
- Simultaneous bioremediation of various contaminants may produce by-products, which are highly toxic to the micro-organisms thereby inhibiting the bioremediation process.

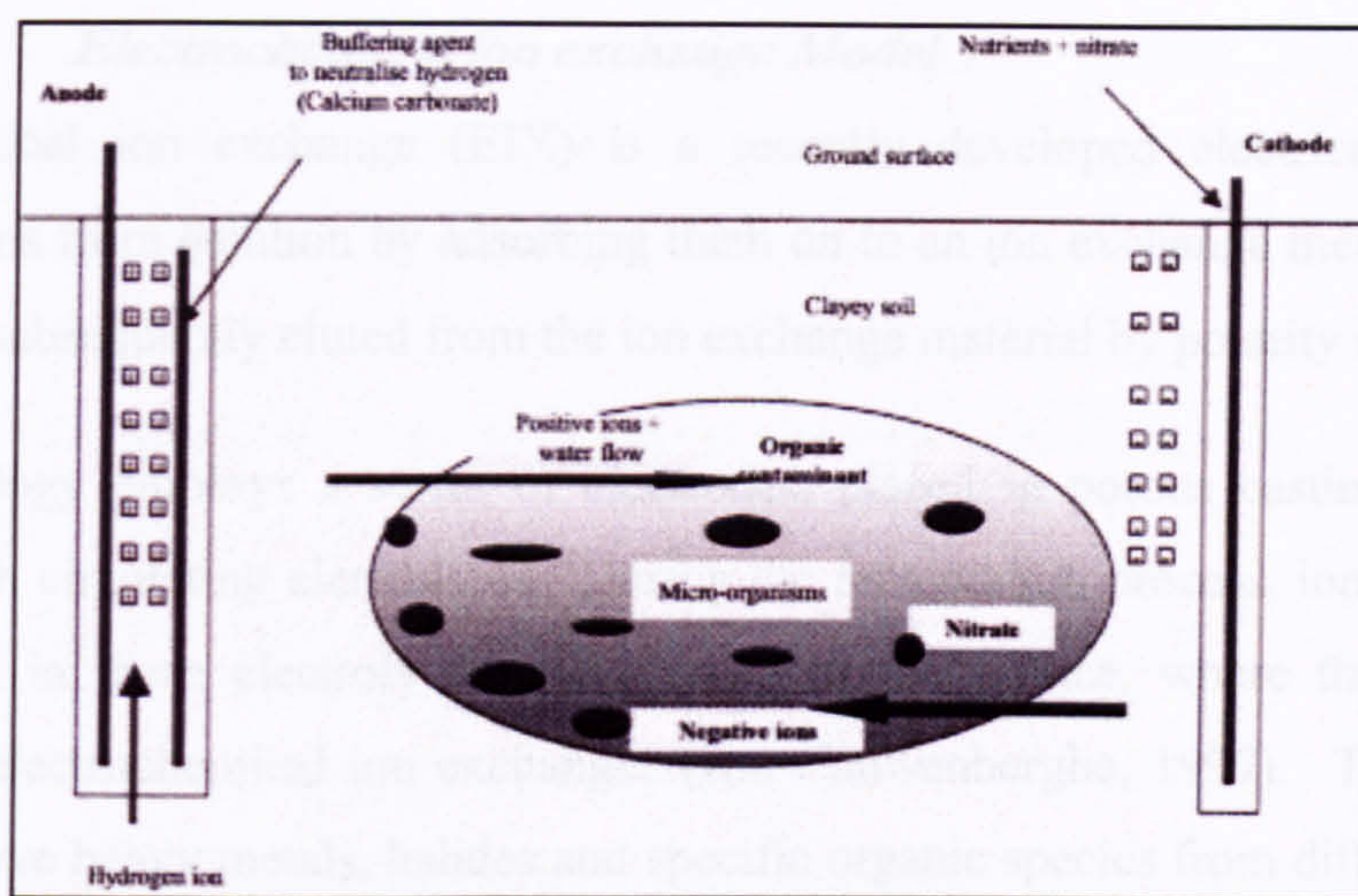


Fig 2.19 Electrokinetic bioremediation, (After Thevanayagam and Rishindran, 1998)

2.3.4.6 ElectroChemical GeoOxidation Model

ElectroChemical GeoOxidation (ECGO) is a patented electrochemical process which uses direct current for the mineralization of organic materials either in-situ or ex-situ in soils and sediments. The ECGO process utilizes a low voltage, low amperage DC current passed between one or more electrode pairs driven into the ground (soil, sediment, sludge, or ground water) to rapidly address a wide range of both organic and inorganic compounds. This current polarizes the soil/sediment, which allows two principal processes for remediation:

- (a) mineralization (destruction) of organic contaminants to their inorganic components (e.g. carbon dioxide and water); and
- (b) Induced Complexation (ECGO-IC) process, which significantly enhances the mobilization and removal of metals contaminants and those radionuclides that behave as metals.

The main advantage of this technology is that there is no need to use catalysts for the oxidation–reduction reactions, because in almost all soils, natural catalysts, such as iron, magnesium, titanium and elemental carbon, are present. The limitations of this technology are the very long remediation time and the lack of proven results.

2.3.4.7 *Electrochemical ion exchange Model*

Electrochemical ion exchange (EIX) is a recently developed electrical process for removing ions from solution by adsorbing them on to an ion exchange membrane. These ions can be subsequently eluted from the ion exchange material by polarity reversal.

This technology employs a series of electrodes, placed in porous castings, which are supplied with circulating electrolytes. During the remediation process, ion contaminants are captured in these electrolytes and pumped to the surface, where they are passed through an electrochemical ion exchanger (van Cauwenberghe, 1997). This method is used to remove heavy metals, halides and specific organic species from different types of soils. The most important limitation of this technology is that it is a very expensive procedure for cleaning effluents containing low levels of contaminants.

2.3.4.8 *Electrosorb™ Model*

Electrosorb™ technology is mostly used in Louisiana, USA, and uses cylindrical electrodes coated with Isolock™ polymer material. Isolock™ is a specifically designed polymer impregnated with pH-regulating chemicals in order to prevent fluctuations in pH (Reddy and Chinthamreddy, 1999). During the remediation process, electrodes are placed in boreholes in the soil and a direct current is applied. Under the influence of the current, ions migrate through the pore water to the electrode, where they are trapped in the polymer matrix. Although there are no indications of the limitations of the technique proposed, it is believed that in order to be commercially available, it should be further investigated, (Virikutyte et al., 2002).

2.3.5 Overview of Electrokinesis Technologies

It is evident that, at present, there is no standardised universal procedure and equipment for the realization of metal electromigration and electrokinetic application in soils remediation approach. Instead there are numbers of technologies (refer to Section 2.3.4 above), each of which have their own operational and design requirements, and limitations. Many of these technologies are technically complex and energy intensive, and geared towards the removal of 90% or more of specific contaminants, under very specific field or laboratory-based conditions. However, in the real environment a low-tech, low-energy contaminant reduction / containment technique may be more appropriate and realistic.

Also, from the review, it has been established that many vendors have marketed the potential of electrokinetic remediation for metals contaminated soils. However, no satisfactory large-scale field demonstration had been conducted yet. Issues such as ability to achieve cleanup goals and by-products formed from additives during electrokinetic remediation, etc., still have not been addressed. Interest in electrokinetic remediation has, of course, been driven by the demand for technologies that are cost effective and can operate in a fine grained soil matrix just as much as they do in coarse grained soils.

For example, despite the numbers of applications that can be listed by some techniques such as LasagnaTM, the applied electrical field technologies have remained non-spread for several reasons (Oyanader-Rivera, 2004). The unavailability of electrode materials that are resistant to corrosion and the poor understanding of the electrokinetic transport associated with the fundamental processes have contributed in part to this status. Studies such as those performed by the US Environmental Agency (US EPA, 2000) clearly state that there is a lack of understanding, among others, of the shape and placement of the electrodes in electrokinetic remediation. These two elements, key for a properly engineered design, when overlooked can considerably affect the movement of ions and therefore the efficiency of removal of pollutants from the contaminated soil. In addition, the determination of the optimal water content in the soil sample is an issue that also needs to be better understood.

It is obvious that enhancement/conditioning chemicals used in some of the schemes in Section 2.3.4, can increase the efficiency of contaminated soil treatment (Section 2.3.3.3); however, there is a lack of data which would clarify further soil and contaminant interactions in the presence of these additives, (Virikutyte et al. 2002).

All these unknowns, to name but a few, suggest that there is a need to refine the electrokinetic remediation technology to come up with a simplistic but efficient method whose electrodes are almost inert, flexible, user friendly and easy to install. At the same time the use of an enhancement agent which is cheap, available and environmentally friendly would be desirable. The current research aims to explore the use of EKGs as electrodes, and de-ionised water as the enhancement/ transporting agent.

2.4 Overview of Previous Research Efforts

This section aims to review the some of the previous laboratory and field researches which have been conducted in reference to the extraction of heavy metals using electrokinetics technology. A summary of the discussion is presented at the end of the section.

2.4.1 Laboratory Investigation

Several recent laboratory studies have been performed to evaluate the feasibility of using the electrokinetic process for removing heavy metal contaminants from soils. In their quest to test the technology, researchers have looked at a wide spectrum of metals spiked in different soils and soil conditions. Table 2.5 presents a summary of some of the selected laboratory work conducted in this area.

Lageman et al. (1990) used the electrokinetic technique for removing different metal contaminants from fine sand and river sludge. The contaminants removed in this study included cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), mercury (Hg), copper (Cu), zinc (Zn) and arsenic (As). Hamed et al. (1991) and Acar et al. (1994) reported on electrokinetic experiments conducted on kaolinite which was contaminated with Pb and Cd, respectively. Pamukcu and Whittle (1992) performed laboratory experiments to investigate the feasibility of electrokinetic removal of cadmium (Cd), cobalt (Co), nickel (Ni), and strontium (Sr) from clays and a sand-clay mixture using different pore fluid solutions. Probstein and Hicks (1993) and Eykholt and Daniel (1994) investigated the removal of Zn and Cu from kaolin, respectively. Lindgren et al. (1992) studied the electrokinetic process for remediating both saturated and unsaturated sand which had been contaminated with large anionic dyes that are similar to chromate ions. Reddy and Shirani (1997) used sodium (Na) and calcium (Ca) as cationic contaminants to investigate electrokinetic remediation of metal contaminated glacial tills. The use of the electrokinetic process for the removal of metallic contaminants from soils has also been investigated by Sah and Chen (1998), who also determined that the electrokinetic process is feasible for removing Cd and Pb from three soils; clay loam, loamy sand and clay. The Louisiana State University (LSU) - Electrokinetics, Inc. Group have also conducted bench-scale testing on remediation heavy metal compounds using electrokinetics. Test results have been reported for Pb, Cd, Cr, Hg, Zn, iron (Fe), and Mg (magnesium).

These investigations proved that the electrokinetic remediation is a significant potential for removing solubilized heavy metals such as As, Ca, Cd, Cr, Cu, Fe, Pb, Hg, Mg, Ni, Na and Zn. They also showed that the contaminants species can be efficiently transported and extracted from the soils tested within the effluent or by electrodeposition or precipitation at or close to the cathode (Hamed et al. 1991; Lageman 1989; Lageman et al. 2004, Probst and Hicks 1993; Reddy and Shirani 1997; Segall and Bruell 1990).

The process can also potentially remove radionuclides from clayey soil samples (Ugaz et al., 1994). Bench-scale tests displayed that uranium (Ur) at 1,000 pCi/g of activity is efficiently removed from kaolinite. A yellow uranium hydroxide precipitate was found in sections close to cathode. Enhanced electrokinetic processing showed that 0.05M acetic acid was enough to neutralize the cathode reaction and overcome Ur precipitation in the soil. Other radionuclides such as thorium and radium showed limited removal (Acar et al., 1992b). In the case of thorium, it was postulated that precipitate of these radionuclides at their hydroxide solubility limits at the cathode region formed a gel that prevented their transport and extraction. Limited removal of radium is believed to be either due to precipitation of radium sulphate or because radium strongly binds to the soil minerals causing its immobilization (Acar et al., 1992b).

Soil Type

Reddy et al. (1997) demonstrated that presence of iron oxides in glacial till creates complex geochemical conditions that retards Cr(VI) transport. The same study showed that presence of iron oxides in kaolinite and Na-montmorillonite did not seem to significantly impact Cr(VI) extraction. Figure 2.20 shows electrokinetic experimental results by Reddy et al. (1997). It is evident that the pH gradient development pattern differed in different soils. The gradient was distinct in the kaolin and Na-montmorillonite. The pH ranged from approximately 11 near the cathode to approximately 2 near the anode. However, the pH gradient observed in glacial till was not as distinct. The pH in glacial till varied from 7.5 near the anode to 10.5 near the cathode. The presence of a high pH environment across the glacial till sample could probably be due to a high buffering capacity of that soil. These pH variations in the 3 different soils had profound effects on the mobility of Cr(VI), and consequently, on the electrokinetic removal efficiency as shown in the same figure above.

Pamukcu and Wittle (1992) and Wittle and Pamukcu (1993) demonstrated removal of Cd, Co, Ni, and Sr from different soil types at variable efficiencies. The results showed that kaolinite, among different types of soils, had the highest removal efficiency followed by sand with 10% Na-montmorillonite, while Na-montmorillonite showed the lowest removal efficiency. The results indicated that soils of high water content, high degree of saturation, low ionic strength and low activity (soil activity describes soil plasticity and

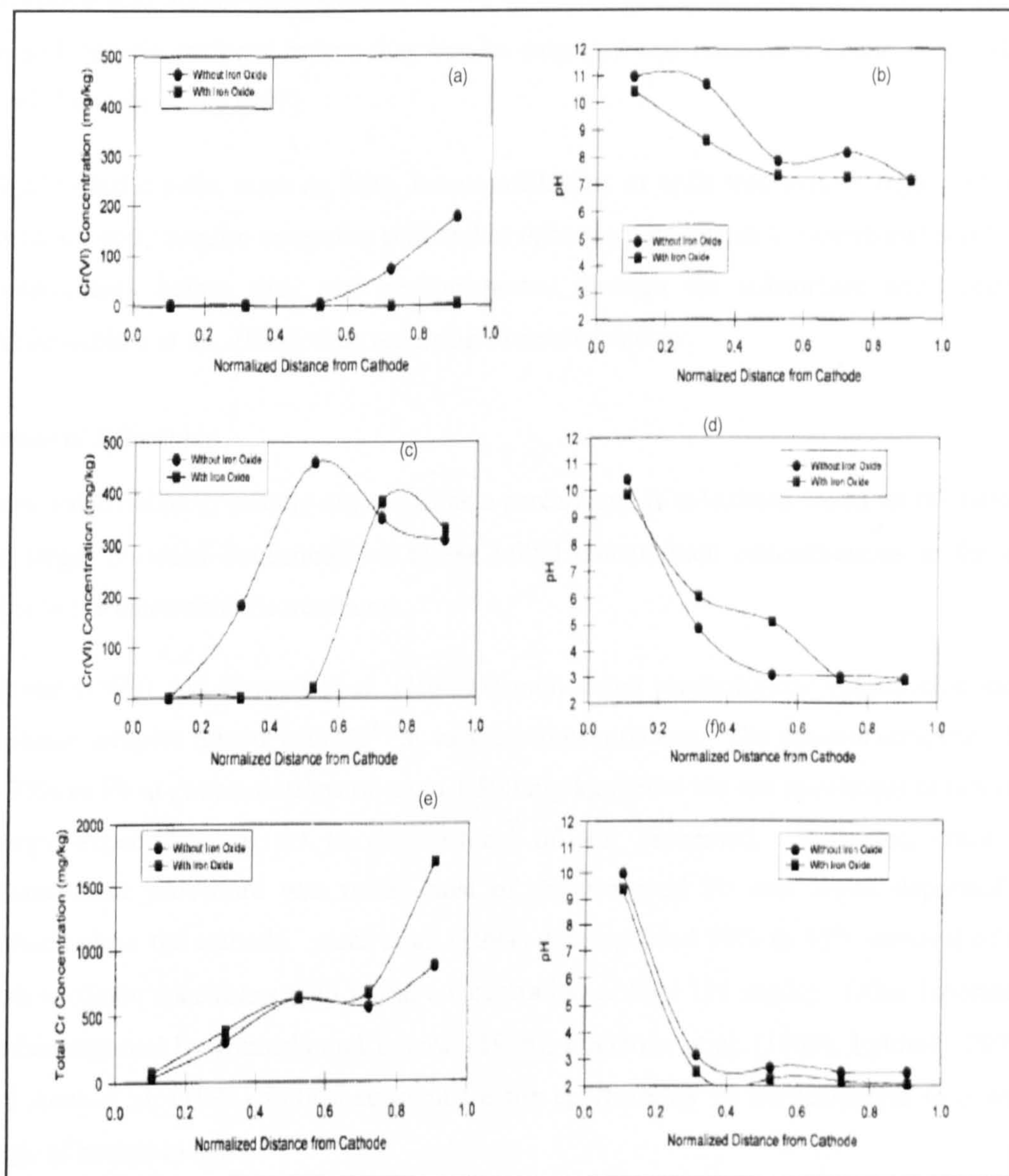


Fig 2.20 *Electrokinetic Experimental Results for Glacial Till (a and b), Kaolin (c and d), and Na-montmorillonite (e and f), (after Reddy et al., 1997)*

equals plasticity index divided by % fines, clay and silt, in the soil) provide the most favourable conditions for transport of contaminants by electroosmotic advection and ionic migration. High soil water content and degree of saturation promote dissolved ion mobility, while low soil ionic strength promotes transport of target contaminants because most of the electric charge will be transferred by the target ions. Soils of high activity exhibit a high acid/base buffer capacity and are able to maintain a positive electro-osmotic fluid flow, that is, from the anode towards the cathode. However, they may require excessive acid and/or enhancement agents to desorb and solubilize contaminants sorbed on soil particle surfaces before they can be migrated and removed (Yeung et al., 1996, 1997; Puppala et al., 1997).

Highly plastic soils, such as illite, montmorillonite, or soils that exhibit high acid/base buffer capacity require excessive acid and/or enhancement agents to desorb and solubilise contaminants before they can be transported through the subsurface and removed (Alshawabkeh et al., 1997), thus requiring excessive energy.

Removal Efficiency

Removal efficiency, usually expressed as a percentage, is calculated based on the ratio of the target remedial concentrations to the initial contaminant concentrations in the soil prior to the electrokinetic treatment.

Hamed (1990) and Hamed et al. (1991) demonstrated electrokinetic remediation using kaolinite samples mixed with Pb^{2+} at various concentrations. The process removed 75% to 95% of Pb at concentrations of up to 1,500 mg/kg across the test specimens at reported energy expenditure of 29 to 60 kWh/m³ of soil processed. However, since no enhancement procedure was used, most of the removed Pb was found deposited at sections close the cathode. Acar et al. (1994) demonstrated 90% to 95% removal of Cd from kaolinite specimens with initial concentration of 99 - 114 mg/kg. Other laboratory studies reported by Runnels and Larson (1986), Lageman et al. (1989), Eykholt (1992), and Acar et al. (1993) further substantiate the applicability of the technique to a wide range of metals in soils.

Lageman et al. (1989) showed that the process can migrate a mixture of different contaminants in soil simultaneously. Lageman (1993) reported 73% removal of Pb at a

concentration of 9000 mg/kg from fine argillaceous sand, 90% removal of As at 300 mg/kg from clay and varying removal rates ranging between 50% to 91% of Cr, Ni, Pb, Hg, Cu, and Zn from fine argillaceous sand. Cd, Cu, Pb, Ni, Zn, Cr, Hg, and As at concentrations of 10 to 173 mg/kg also were removed from a river sludge at efficiencies of 50 to 71%. The energy expenditures ranged between 60 to 220 kWh/m³ of soil processed. Lageman et al. (1989) and Lageman (1993) concluded that the electrokinetic process works on a mixture of contaminants. They predicted, though, that monovalent ions may be removed at a higher rate than higher valence ions. Monovalent ions tend to have a much greater mobility compared to higher valence ions (Spoor 2002) since monovalent ions have lesser influence (or attraction force) on the water molecules in their hydration sphere in comparison with the higher valence ions. This makes the former relatively lighter and can therefore be removed with much greater ease.

Work by Reddy and Shirani (1997) found and also concluded that removal efficiency of the electro process increases when;

- a) the voltage gradient applied to the soil was increased,
- b) the initial concentration of the contaminants was increased, and
- c) the duration of the treatment process was increased.

Reddy and Shirani (1997) also reported that removal efficiency was greater for smaller ions which possess less ionic charge and when the ions existed independently in the soil as compared to when they coexisted.

It should however be noted that the acceptable remedial removal efficiency depends on the initial concentrations and the target remedial concentrations based on the risk analysis (Reddy, 2006).

Contaminant Concentration

Regarding contaminant concentrations, review of data indicated that removal of Cu of concentration up to 10,000 mg/kg of soil and Pb concentration up to 5,000 mg/kg were possible (Alshawabkeh, 2001). Acar and Alshawabkeh (1996) demonstrated extraction of Pb at 5300 mg/kg from kaolinite samples. However, high ion concentrations in the pore fluid increase the electrical conductivity of the soil and thus reduce the efficiency of electroosmotic fluid flow (Gray and Mitchell 1967; Lockhart 1983a,b,c; West and Stewart

1995) – electroosmotic efficiency is defined as the quantity of water moved per unit charge passed (Gray and Mitchell 1967). Moreover, the strength of electric field applied may have to be reduced to prevent excessive power consumption and heat generation during the process. The results of Hamed (1990), Pamukcu and Wittle (1992) and Wittle and Pamukcu (1993) demonstrated that lower initial concentrations of Cd result in higher electroosmotic efficiency; however, removal efficiencies were higher for samples with higher initial concentrations. Alshawabkeh et al. (1997) investigated electrokinetic extraction of heavy metals from clay samples retrieved from a contaminated Army Ammunition site. The soil contained cations at the following concentrations: Ca: 19,670 mg/kg; Fe: 11,840 mg/kg; Cu: 10,940 mg/kg; Cr: 9,930 mg/kg; Zn: 6,330 mg/kg; and Pb: 1,990 mg/kg. The high calcium concentration hindered extraction of other metals. However, the results showed that metals with higher initial concentration, less sorption affinities, higher solubilities, and higher ionic mobilities are transported and extracted faster than other metals.

In general, the presence of a high ionic strength pore fluid, as in the case of very high calcium concentration in the Alshawabkeh et al. (1997) study, delays and hinders transport of target ions (Alshawabkeh 2006). This is because most of the electric charge will be transferred by such ions (e.g. Ca^{2+}) and only a small fraction of the electric current charge will be transferred by the target contaminant. This ratio of how much current is carried by a specific ion is related to the transport number as defined in electrochemistry literature (West and Stewart, 1995).

Electrodes

Both reactive (such as copper) and inert electrodes (in the form of carbon, platinum and graphite plates or rods) have been used in previous studies. Chemically inert but electrically conducting electrodes are preferred since they prevent electrode dissolution and the generation of undesirable corrosion products during the electrolysis process. According to Virkutyte et al. (2002) the most suitable inert electrodes for electrokinetics are graphite, platinum, gold and silver. Acar et al. (1992) however, suggested that these types of electrodes were not cost effective and therefore the need to devise and manufacture cheaper ones, meeting the consideration for the choice of electrode material stated in Section 2.3.3.4, is deemed necessary.

Table 2.5 Summary of Laboratory Data for Electrokinetic Removal of Metal Contaminants

Studies	Soil Type	Contaminant	Type Of Electrodes	Energy used to Decontaminate 1 m ³ of Soil (kWh)	Current Density / Voltage (mA/cm ²) or [V/cm]	Duration / Removal efficiency (hr) / [%]	Set up / Method of Testing	Major Findings
Krizek, et al. (1976)	Slurry / Sediment	Na	-		[0.5 – 1.0]	150 / [-]	Cylindrical 1-D consolidation tests (D = 140mm, L = 250mm)	
		K			[0.5 – 1.0]	150 / [-]		
		Ca			[0.5 – 1.0]	150 / [-]		
Hamnet (1980)	Silica Sand	Na	Carbon Rods	N/A	6.25 – 16.25 [0.6]	12 – 20 [-]	Used a 3-D (35cm by 8 cm with 5cm depth) Lab model	After 12 hours, concentration at anode was a third of the cathode side.
Runnels and Larson (1986)	Silty Sand	Cu	Square Platinum Electrodes (645mm ²)	N/A	0.01 - 0.05 [0.165]	24 – 72 [53]	Used 1-D Cylindrical specimens (D = 1.9cm, L = 15.2cm)	Amount of contaminant removed increased with processing time (total charge passed).
Thompson (1989)	Ottawa Sand	Si Cu			N/A [25]	336 [-]	The middle section that contained the contaminant in solution was sand witched between 2 sections containing the soil specimen	Transport was a function of pH of the soil.
Lageman (1989)	Peat	Pb	Rectangular Electrodes	101		[73]	1-D Lab tests conducted. Pore fluid at anode / cathode compartment flushed with a conditioning fluid intermittently in order to control the chemistry at electrodes	Technology works even on a mixture of contaminants. Removal amount is related to both amount and mobility of specific ion under electrical gradients. Monovalent ions may be removed at a higher rate than higher valence ions.
		Cu		101		[60]		
		Cu		25		[90]		
	Pottery Clay							
	Fine Clayey Sand	Cd		198		[85]		
	Fine Clayey Sand	As		207		[90]		
		Cd				[> 99]		
		Cr		54		[91]		
		Ni		54		[85]		
		Pb		54		[64]		
		Hg		54		[67]		
		Cu		54		[91]		
		Zn		54		[81]		
	River mud	Cd		180		[50]		

Table 2.5 Cont.

Studies	Soil Type	Contaminant	Type Of Electrodes	Energy used to Decontaminate 1 m ³ of Soil (kWh)	Current Density / Voltage (mA/cm ²) or [V/cm]	Duration / Removal efficiency (hr) / [%]	Set up / Method of Testing	Major Findings
Lageman (1989) <i>cont.</i>	River mud	Cu		180		[71]		
		Pb		180		[53]		
		Ni		180		[91]		
		Zn		180		[94]		
		Cr		180		[64]		
		Hg		180		[60]		
		As		180		[66]		
Banerjee, et al. (1990)	Silty/Silty Clay	Cr	Ni-Cu wire mesh electrodes		N/A [0.1 – 1.0]	24 – 168 [93 – 99]	1-D specimens (D = 51mm, L = 25 to 67 mm). Hydraulic and electrical potentials were applied simultaneously to facilitate removal	
Hamed et al. (1991)	Georgia Kaolinite	Pb	Cicular Graphite Electrodes	29 - 60	0.037 [≤ 2.5]	100 – 1285 [70 – 95]	1-D Lab tests performed on Cylindrical specimens (D = 10cm, L = 10cm and 20cm)	Electroplating of Pb(II) at cathode. Removal due to migration advection of acid front generated at anode by the primary electrolysis reaction.
Pamukcu and Wittle (1992)	Kaolinite, Na-montmorillonite, sand-clay mix	Cd, Co, Ni, Sr			[3.94]	24–48 [16.5–95]	-	Soils of high water content, high degree of saturation, low ionic strength and low activity provide the most favourable conditions for transport of contaminants by electroosmotic advection and ionic migration.
Probststein and Hicks (1993)	Kaolinite	Zn	Graphite	40	[1.0]	216 [98]	1-D Lab tests performed on Cylindrical specimens (D = 32cm, L = 20cm)	
Acar et al.(1994)	Kaolinite	Cd	Carbon	50 - 106	0.037 [2.0 –4.5]	716 – 1027 [90 –95]	1-D Lab tests performed on Cylindrical specimens (D = 10.2cm, L = 10.2cm)	High contaminant removal rates are achieved by electromigration than electroosmotic flow when initial pH in the specimen is low.
Acar and Alshawabkeh (1996)	Gergia Kaolinite	Pb	Carbon (D =6.25cm)	700	0.133	2950 [90]	3-D Lab tests performed on W = 91.4cm, H = 91.4cm, L = 182.9cm specimens	When open electrode conditions are used, suction is developed across the soil.

Reddy and Shirani (1997)	Glacial tills	Na, Ca	Graphite (D = 6.2cm)		[0.785 – 1.3]	96 – 504 [22 - 63]	1-D Lab tests performed on Cylindrical specimens (D = 6.2cm, L = 19.1cm)	Ion transport during EK process due to electroosmosis and electromigration. That due to electromigration is significantly higher.
Sah and Chen (1998)	Clay Loam, Loamy Sand, and Clay	Cd, Pb	Graphite (D = 8cm)		[0.44]	168 / [-]	3-D Lab tests performed on W = 5cm, H = 3cm, L = 18cm specimens	The precipitation of both Cd and Pb in the contaminated specimen, during treatment, reduced when 0.1M HCl was added to the soil

According to the literature, no research to-date has been conducted to study the effect of electrode configuration on the efficiency of electrokinetic extraction. Additionally, it was observed in the review, and confirmed by Yeung (2006), that most bench-scale and large-scale laboratory and pilot-scale field studies on electrokinetic remediation performed to date have been one dimensional. In the referred work, electrodes were arranged either horizontally or vertically with the anode and cathode plates, sheets or discs being parallel to each other.

2.4.2 Field Investigations

While the laboratory studies display the feasibility of using electrokinetics to decontaminate soils, limited successful field studies are available, yet it is widely acknowledged that laboratory experiments do not necessarily represent field conditions. Field scale demonstrations of electrokinetic technique are extremely important for identifying and evaluating operational parameters, determining remedial efficiencies for different types of contaminants, and studying the interactions which occur among different contaminants under field conditions.

Lageman et al. (1989), Lageman (1993) and Geokinetics (1998) report the results of full scale field electrokinetics projects conducted in Europe by Geokinetics International. These studies reported removal efficiency of heavy metals ranging from 50% to 91% from various soils and at different concentrations. A summary of five field applications, from the Lageman et al. and Geokinetics investigations, is provided below while the results are summarised in Table 2.6:

1. Electrokinetic technology was employed in remediating a sediment which was dredged from a water-bearing ditch at a former paint factory site. The sediment was distributed 20 - 50cm deep over an area of 70m x 3m and contained lead and copper at concentrations of up to 5000ppm and 1000ppm, respectively. A series of vertical anodes, 2m apart, were installed along a length of 70m, and a horizontal cathode was laid along the length of the site. The remediation efficiency was 70% for lead and 80% for copper after 43 days.
2. Electrokinetic remediation was used at a galvanizing plant which contained sandy clay containing Zn to a depth of 40cm. The contaminant concentration was not uniform and varied from 500 ppm to 3000 ppm. The two cathode drains were

installed at a depth of 50cm below the ground surface and 33 anodes in three rows were installed vertically to a depth of 1m in a test area of 15m x 6m. The current density was 8A/m^2 and the potential gradient was 40 V/m. The removal efficiency was poor, due to a high pH and the presence of ammonia and ammonium chloride in the soil. In these conditions Zn is less soluble.

3. Another pilot project was used to remove Ar at a former wood treatment plant for clayey soil of dimension 10m and 10m x 5m. The highest concentration of Ar was 500 ppm. Cathode drains were installed at a depth of 0.5m and 1.5m below the surface at a mutual distance of 3m. Thirty six anodes were installed at a separation distance of 1.5m between the cathodes. At the beginning of the treatment, the resistivity of the clay and the soil temperature were 10 ohm-metres and 7°C , at a depth of 0.5m. After 4 weeks, the resistivity had changed to 5 ohm-meters, and the temperature had risen to 50°C . The potential gradient was also changed from 40 V/m to 20 V/m to keep a constant current of 4A/m^2 . The cleanup goal of 30 ppm was achieved after 3 months for over 75% of the site.
4. A temporary landfill site was used to receive and treat dredged material contaminated with heavy metals. The contaminated region, which measured 70m x 2.6m x 2.6m, contained soil and sludge which had been contaminated with Cd in concentrations up to 3400 ppm. Cathodes were installed horizontally and anodes vertically. In spite of the presence of cadmium sulphide in the soil in concentrations up to 5000 ppm, the electrokinetic process reduced Cd concentrations to less than 40 ppm in 2 years.
5. Electrokinetic remediation was also reportedly used at an air base where a region measuring 90m x 20m x 2.5m was contaminated with Cu, Pb, Cd, Ni, Cr and Zn. The study reported that after two years of treatment, the concentrations of the metals reduced to acceptable levels.

Table 2.6 Performance Summary of Electrokinetic Soil Remediation Technology Applied at Five Sites in Europe between 1987 - 1994 (after Geokinetics, 1998)

Project	Soil Type	Volume (m³)	Initial Concentration (mg/kg)	Final Concentration (mg/kg)
Former Paint Factory	Peat/Clay	230	Cu > 1,220 Pb > 3,780	Cu < 200 Pb < 280
Operational Galvanizing Plant	Clay	38	Zn 1,400	Zn 600
Former Timber Plant	Heavy Clay	190	As > 250	As < 30
Temporary Landfill	Sand	3060	Cd > 180	Cd < 40
Military Airbase Galvanizing Plant	Clay	1920	Cd 660 Cr 7,300 Cu 770 Ni 860 Pb 730 Zn 2,600	Cd 47 Cr 755 Cu 98 Ni 80 Pb 108 Zn 289

In the United States, field applications of the electrokinetic technology have also been initiated there. US Environmental Protection Agency (1993) reported a pilot scale test site where soils were contaminated with Pb in concentrations of up to 100,000ppm. This test was performed with a current of up to 0.8 mA/cm² across the electrodes placed at a spacing of 2m to 4m. The presence of Ca in concentrations up to 90,000ppm was cited as being responsible for the low efficiency of the electrokinetic process, but in areas where calcium concentrations were low, higher removal efficiencies were obtained.

Another field study reported by Banerjee (1994), from the University of Washington (USA), investigated the feasibility of using electrokinetics in conjunction with pumping to decontaminate a site of Cr. The results of the field study were inconclusive since only the effluent chemistry was monitored and the removal between the electrodes was not investigated.

In 1998, the US Army Environmental Center (USAEC) conducted a field demonstration performance of the technology. This demonstration was conducted at a metals contaminated site at Naval Air Weapons Station Point Mugu, California, (USAEC, ESTCP, 2000). The selected area of study was approximately 2000 m² in and around two former waste lagoons located in the centre of the site. The lagoons were unlined and were used between 1947 and 1978 to receive wastewater discharge from electroplating and metal finishing activities. Surface sampling within the lagoons indicated that levels of chromium and cadmium were up to 25,100 mg/kg and 1,810 mg/kg, respectively. Prior to the field demonstration, extensive laboratory testing was conducted to assess the potential effectiveness of electrokinetic extraction.

The remediation system consisted of electrode arrays made of a series of anodes and cathodes housed in wells. Figure 2.19 illustrates the array of anodes and cathodes that were installed within the test area. The optimum distance between the anodes and cathodes was determined to be 4.3m. The optimum distance between the each anode well in the anode well rows (as well as each cathode well in each cathode well row) was to be 2 m (Hodko et al., 1999).

The electrokinetic remediation system was designed to extract the metal contaminants via electromigration of the contaminant ions and concentration of the ions in the electrode wells. The majority of these contaminants were expected to remain in solution with only minimal plating occurring on the electrodes. Once metal contaminant concentrations had built up in the electrode well, processing of the electrolyte fluid would be conducted to extract the metal contaminants and return the processed electrolyte fluid back to the wells for continued use. This was to minimize the volume of waste generated by the process and resulted in the production of a potentially recyclable material.

The performance goal for the technology was to reduce contaminant levels to California State Total Threshold Limit Concentration (TTLC) and Soluble Threshold Limit Concentration (STLC) levels (USAEC, ESTCP, 2000). However, no contaminants were extracted during the 22 weeks demonstration period. Piezometer well monitoring did not detect any pH effect or mobilized metal contaminants from the artificially confined treatment area during this treatment period.

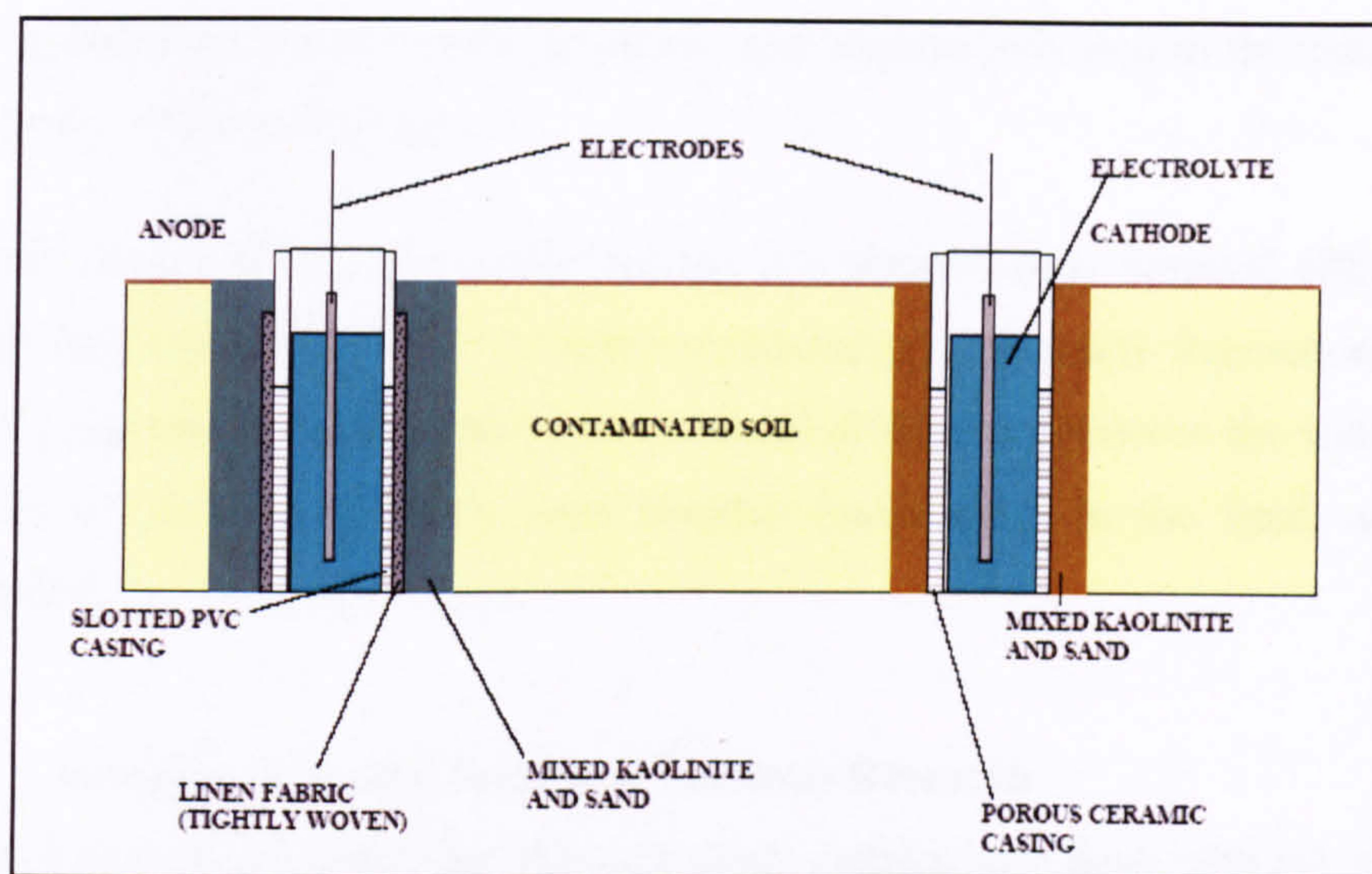


Fig 2.21 Electrode Well Construction (after USAEC, ESTCP, 2000)

This demonstration indicated the importance of conducting bench tests that accurately reflect the effects that site conditions would have on the technology. The bench tests conducted prior to field operations did not accurately reflect the effects that site conditions, specifically the retarding effects that competing ions would have on pH front development and contaminant mobility. Contaminant mobility and pH effects were ultimately observed in the field, however, the duration required for treatment in the field was much longer than anticipated by the bench tests. Also, the bench tests did not reflect the by-product formation that was encountered in the field, specifically the hydrogen sulphide gas and trihalomethane formation.

The site characteristic that most affected the treatment performance was the high chloride concentration of the groundwater. The chloride reactions at the anode acted to retard the development of the pH front, which in turn lengthened the time required to extract the contaminants from the soil. (USAEC, 2003)

The study concluded that electrokinetic remediation heavy metal extraction rate and efficiency is dependent upon many subsurface characteristics such as soil type and grain size, contaminant concentration, ionic mobility, total ionic concentration, types of contaminant species and their solubility, etc. Additional complications with the application of electrokinetic remediation can arise from the presence of organic contaminants and possibly the organic material in the soil. The soil's physical, chemical,

and biological characteristics can individually and cumulatively impact the extraction rate and efficiency of the technology.

Reddy and Shirani (1997) have attributed the low electrokinetic removal efficiencies in most field applications mainly to complex geochemistry, especially interactions with the naturally occurring electrolytes and compositional differences between the soils tested in the laboratory and those which were actually encountered in the field, and mixed contaminants.

2.4.3 Summary from the Review of Previous Research

From this review it is evident that although many authors have dealt with the problem of heavy metals in the past, no standard procedure and equipment for the realization of electrokinetic applications in soils had emerged. However, both recent laboratory and field studies have provided a better understanding of the practicability and feasibility of using electrokinetics to extract heavy metals from soil.

Overall it has been demonstrated that the technology is applicable to soils ranging from silty sands to clays and that the type of metal contaminant does not pose a significant limitation on the technology provided it does not exist in an immobile form, e.g., sorbed on the soil particle surface or precipitated in the soil pore. But despite the apparent success of bench scale tests, the technology has not been widely applied in the field.

In order to improve the technology and establish reliable design data for use in real field conditions, it has been established that there is a need to rethink and redesign bench scale tests which replicate realistic field existences.

The field demonstrations, such as those at NAWS Point Mugu (USAEC, 2003), have identified many discrepancies between the laboratory testing and the performance observed in field applications. As currently designed, the bench tests do not provide an adequate means of predicting performance, duration, and efficiency of the technology. At best most bench scale tests, in their current design, do only provide an indication that contaminants would ultimately be mobilized when the technology is applied.

From Table 2.5 of selected completed studies, over 90 percent of the soil models used were less than a foot (< 0.3048 m) long. In over 15 references, the average volume of the

sample under investigation was about 0.14 m³. The tested specimens were indeed small. The smaller the sample, the more likely it is affected by boundary conditions (among others) which reduce results accuracy.

Of all the bench scale studies reviewed, only work by Acar and Alshawabkeh (1996) reported results with open electrodes (electrodes open to the atmosphere). The rest conducted closed apparatus experiments (assemblies in which the test specimen was closed to the atmosphere). Although Acar and Alshawabkeh research reported that suction developed across the soil when open electrode conditions were used, this literature review however, did not come across sufficient data to adequately compare the two electrode systems. Nonetheless, as had already been discussed, the open electrode system was anticipated to be more representative of the field treatment conditions.

The review of literature indicated that no study had been conducted on the effect of depth on the species removal. Acar and Hamed (1991) indicated that there is no depth limitation in the remediation process. This conclusion is, though, not backed by any studies yet. There is possibility that the soil physical properties such as water content, vary with depth during electro processes. This would then imply that electrokinetics processes would vary with depth, consequently affecting the metal removal. None of the researchers have addressed this in their laboratory studies.

A well-instrumented study would answer these questions and fill this gap. This research was, therefore, set out to bridge the gap between the laboratory and the field.

The unavailability of electrode materials that are resistant to corrosion has also been identified (Oyanader-Rivera, 2004). Inert electrodes such as platinum, gold and silver are prohibitively expensive (Acar et al., 1992). Unlike the electrodes used in the reviewed work, the proposed electrokinetic geosynthetics (EKG) electrodes are cheaper and are technologically engineered to have multi purpose functions as discussed in the following section.

2.5 Electrokinetic Geosynthetics (EKGs)

The section initially defines and describes the concept of EKGs pointing out the advantages of using these materials as electrodes in the electrokinetic process. The different ways in which geosynthetic materials can be made electrically conductive are discussed. The durability of electrodes during treatment of soils is also addressed. Some of the different types of EKGs available are then listed. Lastly, the type of EKG specifically selected for use in the research is discussed.

2.5.1 EKG Concept

The EKG concept combines two well-established technologies of electrokinetics and geosynthetics to create geosynthetic electrodes. EKGs are, therefore, electrically conductive geosynthetics, which, among other functions, are designed to use electrokinetic phenomena in order to improve one or more soil property. This can be achieved in a number of ways including making one or more elements in the geosynthetic conductive or incorporating a new material to perform this function. As such EKGs have pushed the evolution of geosynthetics into a fourth generation (Electrokinetic Ltd, 2005):

- 1st generation – where natural textiles and fabrics were used on an ad-hoc basis during construction.
- 2nd generation – Synthetic textile and fabric materials were used on an ad-hoc basis during construction.
- 3rd generation – Specifically designed synthetic textiles used for target ground engineering functions such as drainage, separation, reinforcement, containment and filtration.
- 4th generation – Composite geosynthetics designed to combine 3rd generation passive functions with active and controllable electrokinetic functions.

The first successful demonstration of the use of electrokinetic technology for soil remediation was performed in the Netherlands in 1986 (van Cauwenberghe, 1997). However, the widespread in-situ application of the process has been prevented because of

a variety of problems, some of which are linked to the available electrodes. The limitations related to the available electrodes include:

- Corrosion of the anodes,
- Difficulties in removing contaminated water and gases from the electrodes,
- Poor electrical contact of electrodes with the soil,
- The cost of producing functioning electrodes,
- Impracticality of polarity reversal, and
- Limitations related to the physical form of the electrodes.

Many of these historical limitations have been eliminated by the introduction of EKG. The concept of the combination of electrokinetic phenomena with chemically inert geosynthetic materials has greatly reduced the problem of electrode corrosion and, owing to the design of the EKG electrodes, current density and electrical contact with the soil are dramatically improved.

By forming the electrode as a geosynthetic, EKG overcomes the problem of removing electroosmotically gathered water by utilising the drainage function of geosynthetics and it provides the additional advantages of exploiting geosynthetics' reinforcing and filtration characteristics and their ability to take on a wide variety of shapes and forms.

Furthermore, because the electrodes can be made identical, they can function equally efficiently as either cathode or anode, making polarity reversal easy to implement with EKG.

For these reasons, EKGs are considered to be ideal materials for the treatment of contaminated land using electrokinetics.

2.5.2 Electrically Conductive Materials that can be used for EKGs

There are various electrically conductive materials which could be used to form geosynthetics and are discussed in the following subsections.

2.5.2.1 *Intrinsically Doped Polymers*

Doped polymers can be produced by electrical or chemical deposition, e.g. polybithiophene,. However, these organic conducting polymers are not particularly stable, and are quickly attacked by oxygen and water, a process in which the double bonds are attacked and the compound hydrolysed (Nettleton 1996).

Spun Polypyrrole is a relatively cheap material that has an electrical conductivity of 100 S/cm. This polymer is, however, very brittle and would require supporting on some other material such as polyethylene terephthalate (PET) or Polymethylmethacrylate (PMMA) (Campbell 1994).

2.5.2.2 *Carbon Filled Polymers*

Carbon filled polymers are produced by the addition of conductive carbon black powder to conventional polymers. Conductive carbon black powder is a high structure (long carbon chains) very fine particulate powder formed from the controlled burning of hydrocarbons. Virtually all thermoplastics can be compounded with carbon black powder (Wright and Woodham, 1989). As the concentration of carbon black powder added to the polymer base increases, its electrical conductivity increases until the polymer becomes conductive, as show schematically in Figure 2.22 (Pugh 2002).

When carbon black is added to a polymer the physical strength properties are generally reduced with the degree of loss being proportional to the concentration of carbon black added. The higher the concentration of carbon added, the lower the strength of the composite material. In these composites it is the carbon filler which conducts electricity and not the polymer. If carbon black is used as the filler then a loading of between 20% - 30% by weight will be required to produce a suitable conductive polymer (Jones et al., 1996).

2.5.2.3 *Carbon Fibres*

Pure carbon fibres are more conductive than carbon filled polymers, but are more difficult to process. For example, carbon fibre rolled crystals are good stable conductors, but are stiff and brittle (Nettleton 1996). Also, when large voltages are applied to polymers that use carbon as the conductive medium, carbon oxidises to liberate carbon monoxide and dioxide at the anode as illustrated in Equations 2.4 and 2.5 (Eastwood 1997):

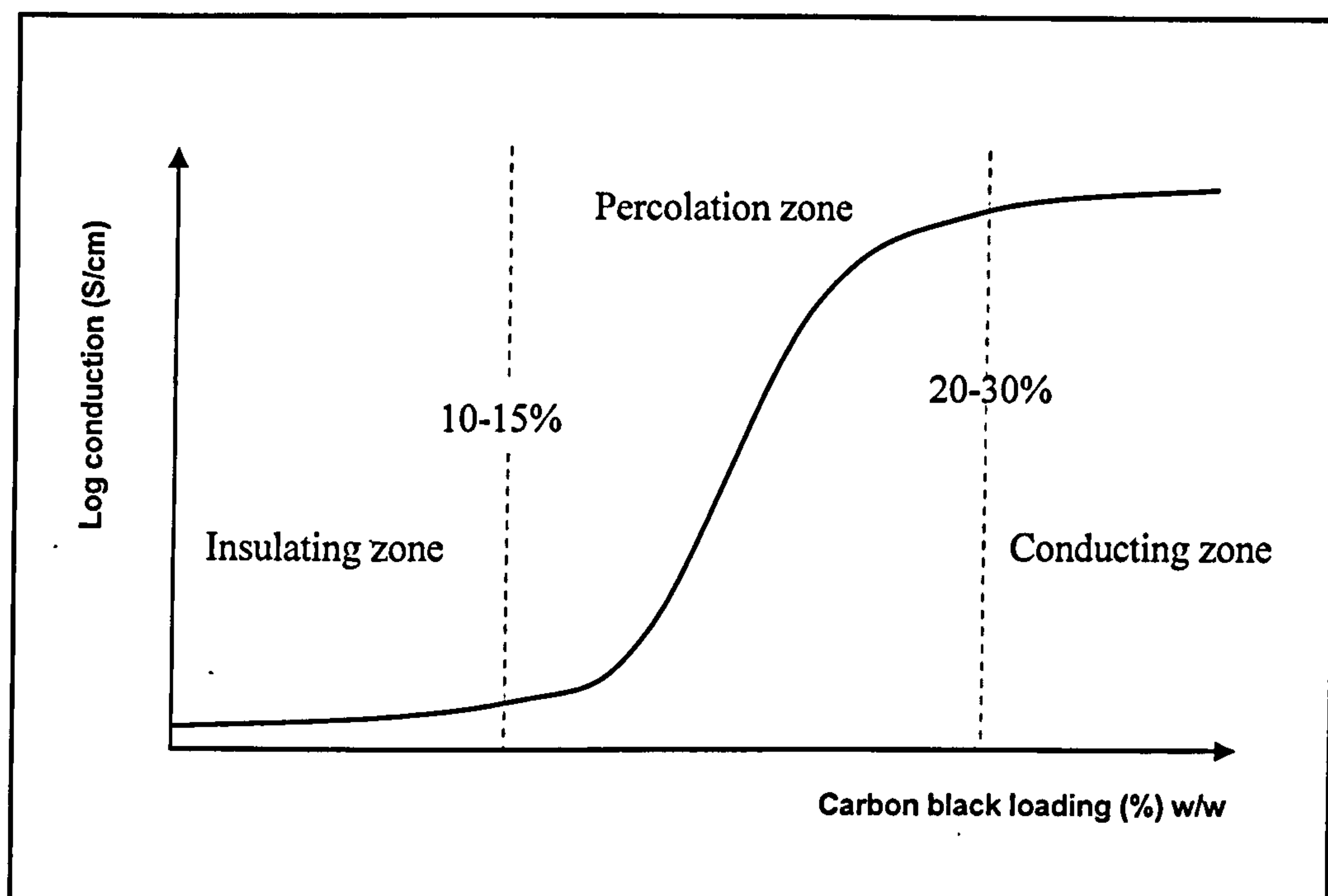


Figure 2.22 Schematic of Conductivity against Carbon Black Loading For Thermoplastic (After Pugh 2002)



However, the addition of common salt (sodium chloride) at the anode can prevent this. The other issue of concern is that in low pH (at less than 4) environments carbon is oxidised, and if there is sufficient loss of carbon (40% percolation) voids may form in the structure (Nettleton 1996). This results in an increase in the surface electrical resistivity of the polymer due to the decrease in the carbon content and due to the presence of voids forming on a microscopic scale. The dissolution of the carbon from the surface also further exposes carbon located more deeply within the polymer structure to dissolution resulting in the overall reduction in conductivity. These problems would also exist with a carbon filled polymer. However, at the low voltages used for electrokinetic process this problem is unlikely to be significant (Pugh, 2002).

2.5.2.4 *Metallic Fibres*

Metallised fibres or metal-coated fibres can be incorporated into the manufacturing process particularly if the material is formed by needle punching or weaving. Metal-coated fibres have a low electrical conductivity ($10^{-6} - 10^{-1}$ S/cm) and are unsuitable for use in EKGs (Pugh, 2002). However, the metal and metallised fibres are considered suitable, although their durability under anodic conditions is likely to be poor, unless chemically inert and electrically conducting metals are used (Section 2.3.3.4).

2.5.3 *Durability of the Electrode Materials*

During electrokinetic process, chemical reactions take place at both the anode and cathode as discussed in Section 2.3.2. If the anode material is not chemically inert, the anodic reactions result in the electrode's consumption giving it a finite life. Therefore, the service life of the anode is dependant upon the material that is used to make it.

In Table 2.7 below, typical corrosion rates for three commonly used anodic materials are presented. It is shown that electrodes made from carbon would have the lowest degradation rate. The apparently low consumption rate of carbon quoted appears to be as a result of its low molecular mass and the requirement of $4e^-$ for the oxidation of each carbon atom (Eastwood 1997), i.e. more electric current is passed per oxidation of each atom.

The typical corrosion rate of $0.5 \text{ kg A}^{-1} \text{ year}^{-1}$, for the consumption of carbon, is believed to be representative of the degree of corrosion for electrodes made from carbon operating at current densities of up to 10 Am^{-2} (Pugh, 2002).

Table 2.7 Corrosion Rates for Common Anodic Materials (Eastwood 1997)

Anode Material	Atomic Mass	Oxidation Reaction	No. Of Electrons	Stoichiometric Predicted Consumption ($\text{kg A}^{-1} \text{ year}^{-1}$)	Typical Corrosion Rate ($\text{kg A}^{-1} \text{ year}^{-1}$)
Iron	55.85	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	2	9.1	9.0
Aluminium	26.98	$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$	3	2.9	4.5
Carbon	12.01	$\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4e^-$	4	1.0	0.5 – 2.0

Chemically inert but electrically conducting materials have also found use or have been specifically developed for anode materials. These include the naturally occurring noble metal platinum (Pt), gold (Au), magnetite (iron oxide Fe_3O_4), other metal oxides and the conductive ceramic Ebonex (Atravee 2005). These materials are able to withstand significantly higher current densities with only a negligible, if any, consumption rate. However, they are prohibitively expensive (Virkutyte et al., 2002).

2.5.4 Types of EKGs

There are possibly as many types of EKGs as there the number of manufacturers. However, those developed for use as electrodes at the University of Newcastle upon Tyne, could broadly be grouped into three major types (Rowe and Jones, 2000). They include:

2.5.4.1 Type 1 - EKG

This is a conventional woven geotextile fabric with conductive thin metallic or carbon black elements incorporated into or stitched on the matrix (Figure 2.23). Although not specifically designed as an EKG, its use shows the widespread easy application this method could have. The finished fabric is soft, flexible and permeable whilst retaining its strength and durability.

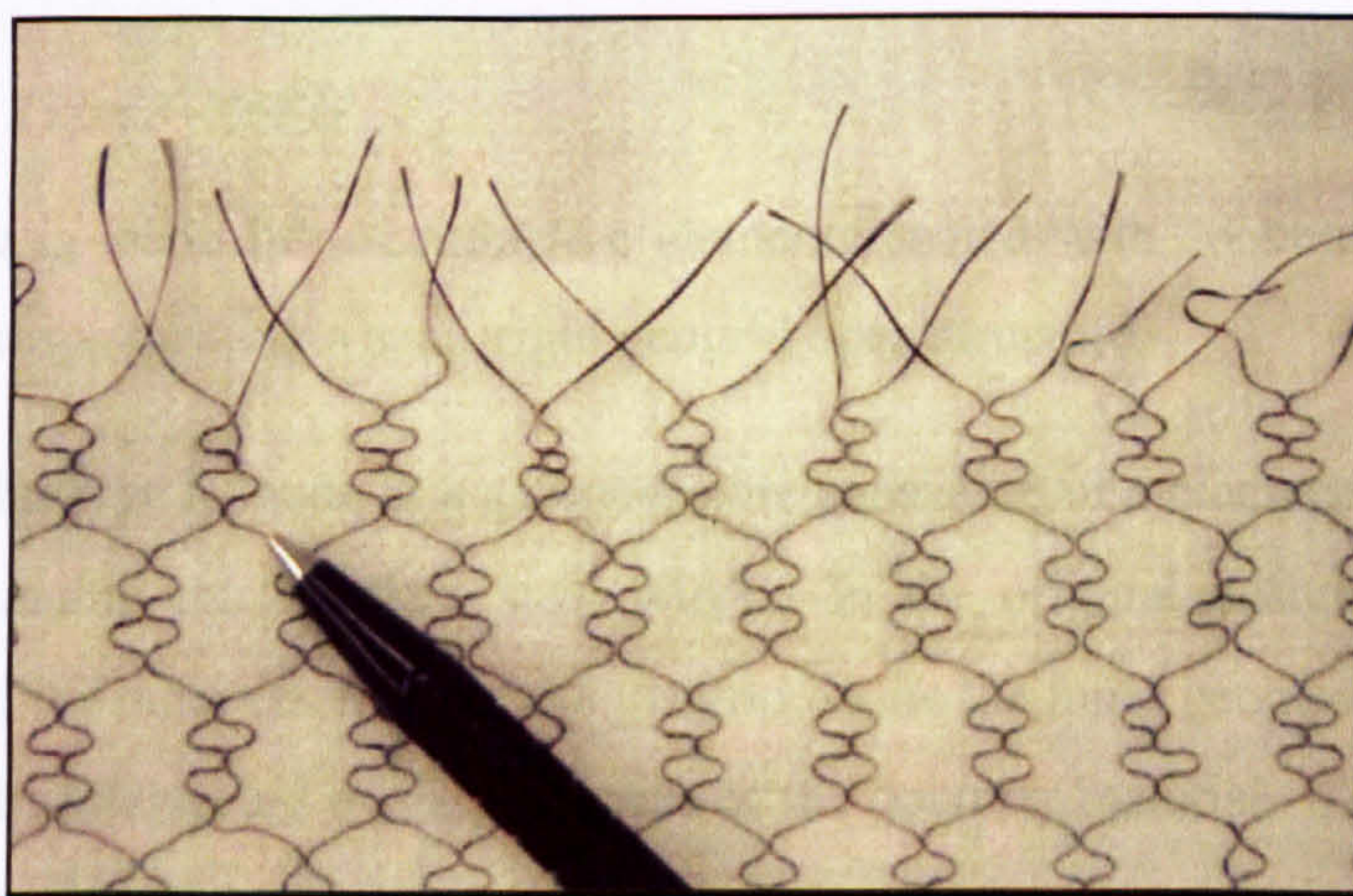


Fig 2.23 Example of Type 1 - EKG

2.5.4.2 Type 2 - EKG

This is a needle-punched non-woven geotextile material made from inert polymeric and conductive fibres (as fillers) forming a composite sheet of uniform thickness (Figure 2.24). The fillers can be made of carbon black fibres or finely divided metals. A higher percentage of these conductive elements results in a more overall conductive material.

Generally, the material is soft, flexible and permeable. Its close needle-punched structure enables the material to double as a filter and electrode at the same time. This material is fairly weak and can easily be ripped apart when stretched by hand.



Fig 2.24 Example of Type 2 - EKG

2.5.4.3 Type 3 - EKG

This EKG type is made from conductive elements coated with conventional polymeric reinforcement strips forming a semi-rigid geogrid open structure.

The most popular type is made of a geomesh core consisting of a black conductive carbon polymer surrounding the stainless steel wires. In the original design, a fabric filter material formed the outer covering of the geogrid, while the inner geomesh core consisted of horizontal ribs intersected by diagonal ribs of the polymer material. The geogrid EKG was manufactured with a circular hollow cross-section in a wick-drain like manner designed for use as a combined well-cathode. Figure 2.25 below shows the schematic diagram of this EKG type.

2.5.5 EKG used

Any of the above types EKGs could have been used as an anode or cathode electrode. But for the purpose of remediation and ease of installation, this study used the Type 3 EKG also known as the Netlon EKG. The selection of this type of EKG was also based on its form which was thought to make it more potentially suitable for in situ treatment of contaminated land. However, there could be a variety of different forms that could be designed to meet the specific needs of any site, method of treatment, etc.

The Netlon EKG used was originally developed under EPSRC Contract No. GR/K20590 (Nettleton 1996) as an electrically conductive band drain, and consisted of an electrically conductive geonet core surrounded by a thermally bonded non-woven filter fabric (TERRAM 1000). The specific design was patented by Netlon Limited under Patent application GB 2327686 A (Netlon Ltd 1998). In this study, in order to reduce the resistance of the test cell by having the conductive elements directly in contact with the contaminated soil specimens, the non-woven filter fabric wrap was removed leaving the geonet as shown in the inset in Figure 2.25.

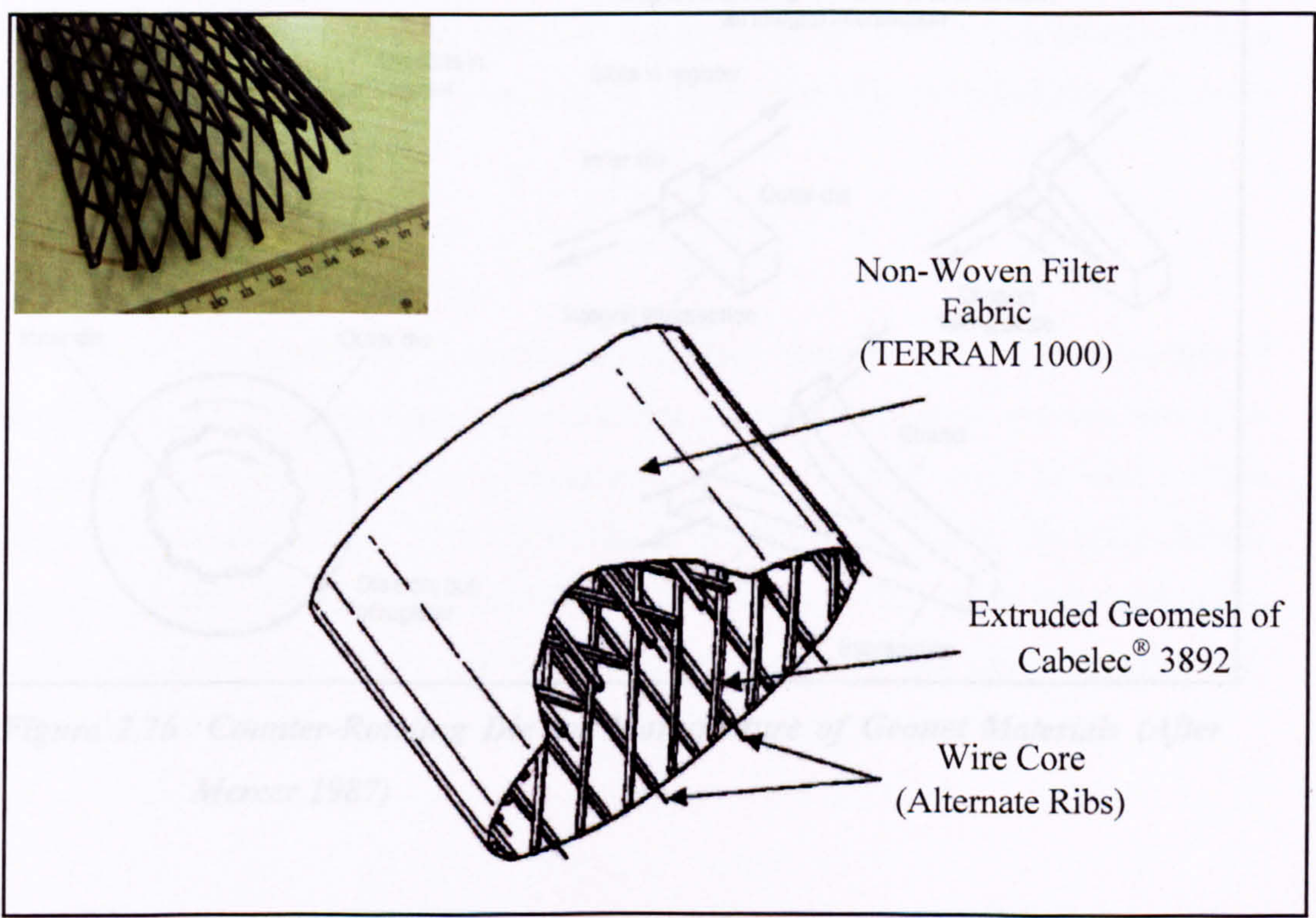


Fig 2.25 Type 3 EKG (After Netlon Ltd 1998)

The geonet was made from conductive elements of a Cabelec[®] 3892 polymer. The elements were formed into a mesh ‘sock’ using the counter-rotating die method as shown in Figure 2.26. The Cabot Cabelec[®] 3892 polymer was a specifically formulated conductive compound based upon conductive carbon black dispersed in a modified high density polyethylene resin (CABOT 1997) i.e. a carbon filled polymer (refer to Section 2.5.2.2). The polymer was specifically designed for extrusion applications, and was developed for the minimisation of electrostatic discharge hazards in electro-statically sensitive environments. Additionally, it made the EKG more physically and chemically robust. The overall configuration was almost inert and therefore resisted the corrosion problems that plagued earlier attempts to exploit the principle of electrokinetics. The material properties for Cabelec[®] 3892 are given in Table 2.8.

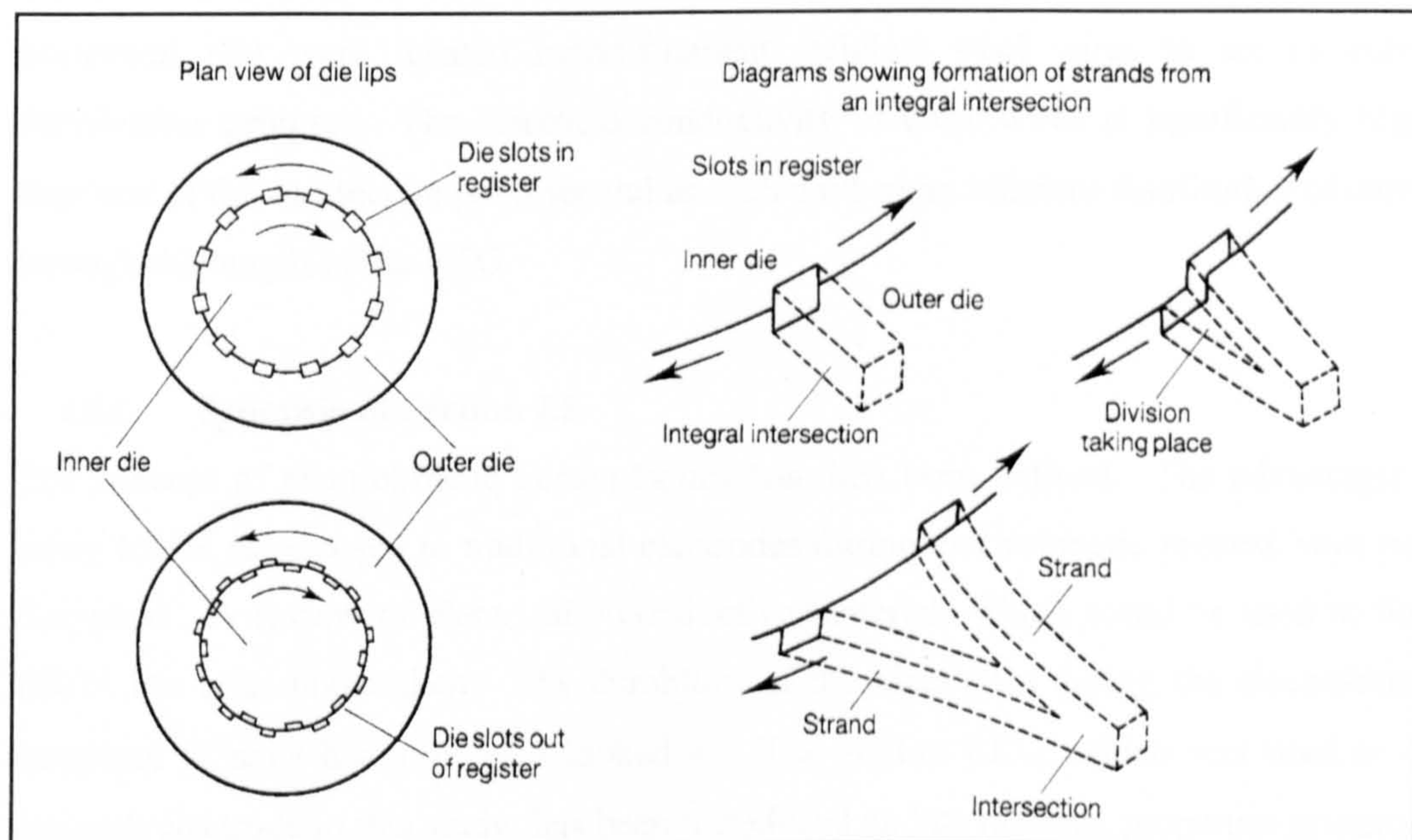


Figure 2.26 Counter-Rotating Die for Manufacture of Geonet Materials (After Mercer 1987)

Table 2.8 Physical properties of Cabelec® 3892 (After CABOT, 1997 and Netlon Ltd, 1998)

Property	Test Method	Value
Density @ 23°C	ISO R1183	1063 Kg/m ³
Volume resistivity	CABOT – D007B	4*10 ² Ωcm
Surface resistivity	CABOT – D042C	10 ³ Ω/sq
Tensile strength at break	ISO 527	18 MPa
Tensile strength at yield	ISO 527	25 MPa
Elongation at break	ISO 527	160 %
Surface resistivity *	CABOT –D042D	5x10 ² Ω/sq

Note: * Typical value for CABELEC® 3892 obtained on 0.4mm- thick extruded tape.

During the manufacturing process, the extrusion process consisted of keeping the outer die-head stationary and rotating the inner die-head, such that the geomesh produced consisted of horizontal ribs intersected by diagonal ribs. At the centre of alternate horizontal ribs were located mono-filament stainless steel wires to act as current distribution stringers. The electrical conductivity of these wires is significantly higher than that of the conductive polymer and as such gave more efficient distribution of current through the length of the EKG.

2.5.6 Synopsis of Section 2.5

The concept of electrokinetic geosynthetics has then been defined. The advantages of using EKGs as opposed to traditional electrodes during electrokinetic process have been discussed. A review of electrically conductive materials which could be used to form EKGs has been undertaken. The durability of the electrodes during the electrokinetic treatment of soils has also been looked at. The Netlon EKG, which was used as the research electrode in this study, has been introduced and its material properties presented. Further justifications for selecting this type are given in the next chapter.

RESEARCH OBJECTIVES AND HYPOTHESIS

3.1 Research Objectives

The overall aim of the study was to determine the feasibility of extracting heavy metals from contaminated fine soils using electrokinetics technology with electrokinetic geosynthetics (EKGs) as electrodes. The aim was, more specifically, to demonstrate the effectiveness of using EKGs in enhancing the removal of zinc from kaolin with and without flushing with deionised water.

In order to achieve the aim, the following objectives were to be met using the laboratory scale models of the treatment process:

- a) Determine the temporal changes in current during experimentation and its influence on the changes in water flow, water content and contaminant movement and extraction, as well as the effect of current intermittence.
- b) Determine the relationship with time of the amount of the Zn^{2+} extracted along both the length and vertical depth of the cell with and without flushing of deionised water.
- c) Determine the spatial changes in water content on the effectiveness of contaminant removal.
- d) Determine whether maintaining a stream of clean water in channels directly installed in the contaminated soil enhanced metal removal.
- b) Evaluate the temporal and spatial variation in pH during electroosmosis and its influence on contaminant removal.

3.2 Research Hypothesis

From the review of the theory, two electrokinetic processes were highlighted as the primary mechanisms by which contaminants are transported through the soil towards one or the other electrodes. They were electromigration and electroosmosis. Of the two, electromigration of solubilized ions was considered the main mechanism of transportation

of the positively charged metallic ions towards the cathode. During electromigration, laboratory research treatability studies (Acar and Alshawabkeh, 1993; Reddy and Shirani, 1997; etc.) indicated that the majority of the metal contaminants would be solubilized in the pore water as a result of the pH fronts generated by the process of hydrolysis at the electrodes. However, previous field experiences and some bench scale experiments showed that uncontrolled and unmanaged electromigration of H^+ and OH^- ions resulted in metals precipitating out of solution hindering the removal of metal contaminants from the soil. This caused a hindrance to the extraction operation. In these circumstances, it is necessary to inject reagents into the soil to enhance solubilization and transportation of metal contaminants. Three types of flushing solvents could be considered as agents for solubilization of the metal contaminants; acids, alkalis or simply a neutral conditioning fluid such as pure water. In-situ flushing with acids has several drawbacks. For instance, the acid could cause too much dissolution of soil minerals resulting in an excessive release of some soil constituents, such as aluminium and silicon (Acar and Alshawabkeh, 1996; Acar and Alshawabkeh, 1997; Acar et al., 1996). Also, improper use of some acids in the process may pose a health hazard. For example, the use of hydrochloric acid may: increase the chloride concentration in the groundwater, promote the formation of some insoluble chloride salts such as lead chloride, and if the chloride ions reach the anode, chlorine gas will be generated by electrolysis (Alshawabkeh et al 1999).

Alkalis on the other hand have not been tested and approved since most metals precipitate in high pH environments (Section 2.3.2.4). Further more, enhancing chemical agents (acidic or alkali) injected into the soil to improve the efficiency of the cleanup process complicate the soil-contaminant interactions (Eykholt and Daniel 1994; Cox et al. 1996; Virkutyte et al. 2002). An improper choice of enhancement agent may, therefore, aggravate the contamination problem and make the remediation process much more difficult (Yeung et al., 1996). Water being a universal solvent, simple in chemical composition (H_2O), and an environmentally friendly media was proposed as the cheap alternative agent for this task. This study, specifically, selected deionised water (water that has had ions or dissolved solids removed by the ionic exchange process) as the flushing agent.

3.2.1 Approach

Two electrokinetic remediation removal approaches were identified for investigation: One Process Approach and Two Process Approach.

One Process Approach (also referred to as closed anode) was to be achieved by electrokinetic migration of metal contaminants towards the cathode electrode. Once the EKG electrodes were installed vertically direct in the soil specimen, and electrically energised, electromigration of metals was expected to take place without any external enhancement agent.

Two Process Approach (open anode) was to be achieved by combining soil flushing and electrokinetics processes. While the electro migration process was underway, water would be availed at the anode so as to maintain a constant electroosmotic flow. Instead of flushing with acid or alkali solvents, deionised water was to be used. Electroosmotic transport of dissolved contaminants through treatment zones placed between EKG electrodes was expected to occur once the power was switched on. The movement of target ionic species would be enhanced by the continuous stream of water coming from the anode.

In both approaches, once the contaminant was dissolved in the pore water, and as the water molecules moved in the direction of the cathode under the influence of the electrical field, it was anticipated that the soil water would drag along the dissolved metallic ions. This would concentrate the contaminants towards the cathode electrode for subsequent removal. Once the metallic species were at or near the electrode, the contaminated fluid would then be recovered by pumping it from the cathode section or allowing it to drain into the effluent chamber.

It was expected that the process would produce a greater degree of contaminant removal under the Two Process Approach. Hence, a greater emphasis (in terms of the monitoring process as well as the number of tests conducted) was placed on enhanced removal under this approach. It was hoped that, with all other factors kept constant, the higher the water content of the soil specimen the greater the magnitude of the electroosmotically induced flow. A higher flow rate would consequently result in an increased mobility of the dissolved ionic contaminants.

Figure 3.1 below illustrates the expected water flow patterns generated by electroosmotic forces. It was considered that as the electroosmotic water moves across the plume of contamination, it would wash the dissolved metallic cations towards the cathode wells for removal.

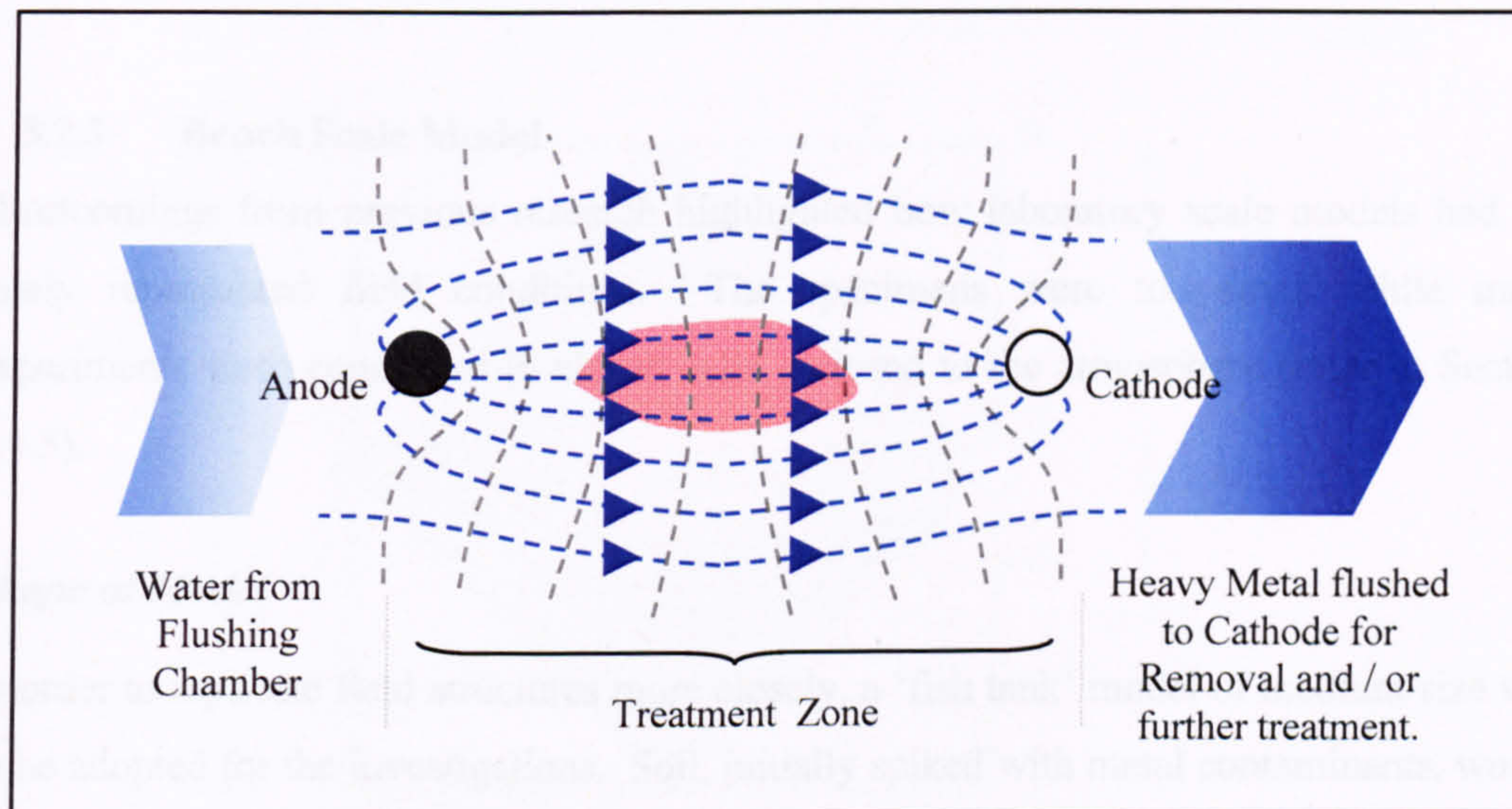


Fig 3.1 Sketch of Flow-net across Plume of Contamination

3.2.2 Purpose of the Flushing Water

Because the dissolved heavy metals ions are positively charged, it was likely that remediation would start from the anode end of the cell. Gradually the cations would be transported to the cathode where they would be drawn out through the purge water. Therefore, clean deionised water would be injected continuously into the anode and driven toward the cathode by electroosmosis. The contaminated water would then be removed from the well points created at the cathode end of the cell.

It was also anticipated that the constant water supply from the anode would control the pH within the cell by causing the H^+ ions generated at the anode to advance at a faster rate towards the cathode. In the process this would assist in desorption of metal species and dissolution of the hydroxides. The low pH across the cell would also prevent the premature precipitation of the metal ions within the soil.

Additionally, during electroosmotic migration through the soil, movement of the water depletes soil water adjacent to the anode, while water collects near the cathode. As the water content decreases at the anode, the soil conductivity becomes too low for the electrokinetic remediation application (Mattson and Lindgren, 1995). Therefore the flushed water also serves as a conducting medium to maintain the electric current and facilitate migration.

3.2.3 Bench Scale Model

Shortcomings from previous research highlighted how laboratory scale models had not truly represented field conditions. The specimens were too small while many experiments were conducted in closed cells – closed to the atmosphere (refer to Section 2.4.3).

Shape of Model

In order to replicate field structures more closely, a ‘fish tank’ model of medium size was to be adopted for the investigations. Soil, initially spiked with metal contaminants, would be placed into the fish tank. The EKG electrodes were then to be installed directly into the soil specimen and an open structure (where the test specimen is exposed to the atmosphere) maintained throughout the experiment. Consequently, the gases generated at both electrodes, in the open structure, would escape freely to the atmosphere without any entrapment. Entrapment of gases especially around the electrodes increases the cell resistivity consequently hindering the contaminant migration. Depending on the approach, deionised water would or would not be continuously fed at the anode.

Dimensions of the Model

Alshawabkeh et al., (1999) and Alshawabkeh (2001) were able to come up with an approximate and practical approach for showing the electric field distributions between electrodes thereby enabling the evaluation of the area of effective and ineffective electric fields. The ineffective spots are areas of inactive electric field during the electrokinetic process.

The analysis of the electric field distributions by Alshawabkeh and his team showed that the ineffective area for an electrokinetic cell has the shape of a curvilinear triangle. The

height of this triangular area is approximate and depends on processing time, electrode spacings, and alignment. For a 1-D application, with the width of the cell equal to the anode-cathode spacing, the triangle height approximates to half the distance between the two electrodes as shown in Figure 3.2.

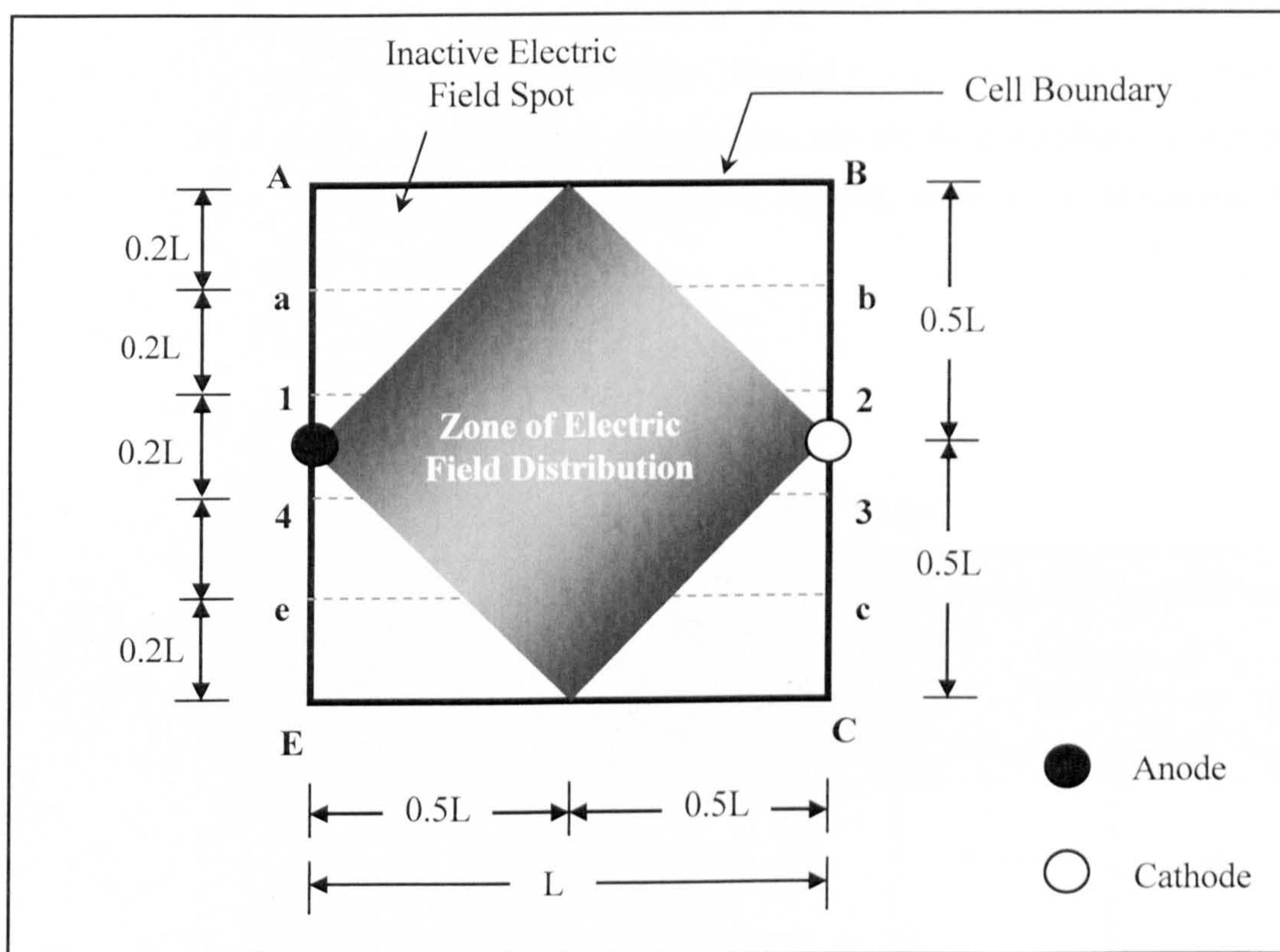


Fig 3.2 Approximate Evaluation of Ineffective Areas for 1-D Electrode Configurations (after Alshawabkeh et al., 1999b; Alshawabkeh, 2001).

Efficient remediation application requires optimizing the process by adopting the best electrode configuration and spacing, since electrode requirements clearly affect the uniformity of electric fields and development of ineffective areas. To minimise the development of inactive electric field, in the 1-D case, it would require increasing the number of anodes and cathodes on either side. This inevitably increases the cost of the process. For example, decreasing the same-polarity electrode spacing to one half the anode-cathode spacing can decrease the area of ineffective electric field by one-half, but would result in a 100% increase in electrode requirements (Alshawabkeh et al., 1999). In

a bench scale model situation, however, the development of ineffective spots can be reduced by decreasing the width of the cell.

Using the approximations proposed by Alshawabkeh, calculations of the percentage of ineffective area for three configurations of different cell widths (while maintaining the same anode-cathode distance) are summarized in Table 3.1. The computations are based on the assumption that if the cell boundaries are adjusted to 1-2, 3-4, a-b and c-d, (refer to Figure 3.2) the resultant confines would not affect the electric field distributions between the two electrodes. This assumption provides a practical method for comparing the efficiency of the different configurations.

Table 3.1 Impact of Cell Width on Size of Ineffective Areas

Configuration of Cell	Electrode Spacing	Width of Cell	Area of Cell (A_{cell})	Computed Ineffective Area (A_{ine})	
				(A_{ine})	% of A_{cell}
ABCD	L	L	L^2	$0.50L^2$	50
abcd	L	0.6L	$0.6L^2$	$0.18 L^2$	30
1234	L	0.2L	$0.2 L^2$	$0.02L^2$	10

From Table A3.1, the cell area of ineffective electric field (as a percentage of the total cell area) is plotted against the ratio of the cell width to the anode-cathode distance in Figure 3.3.

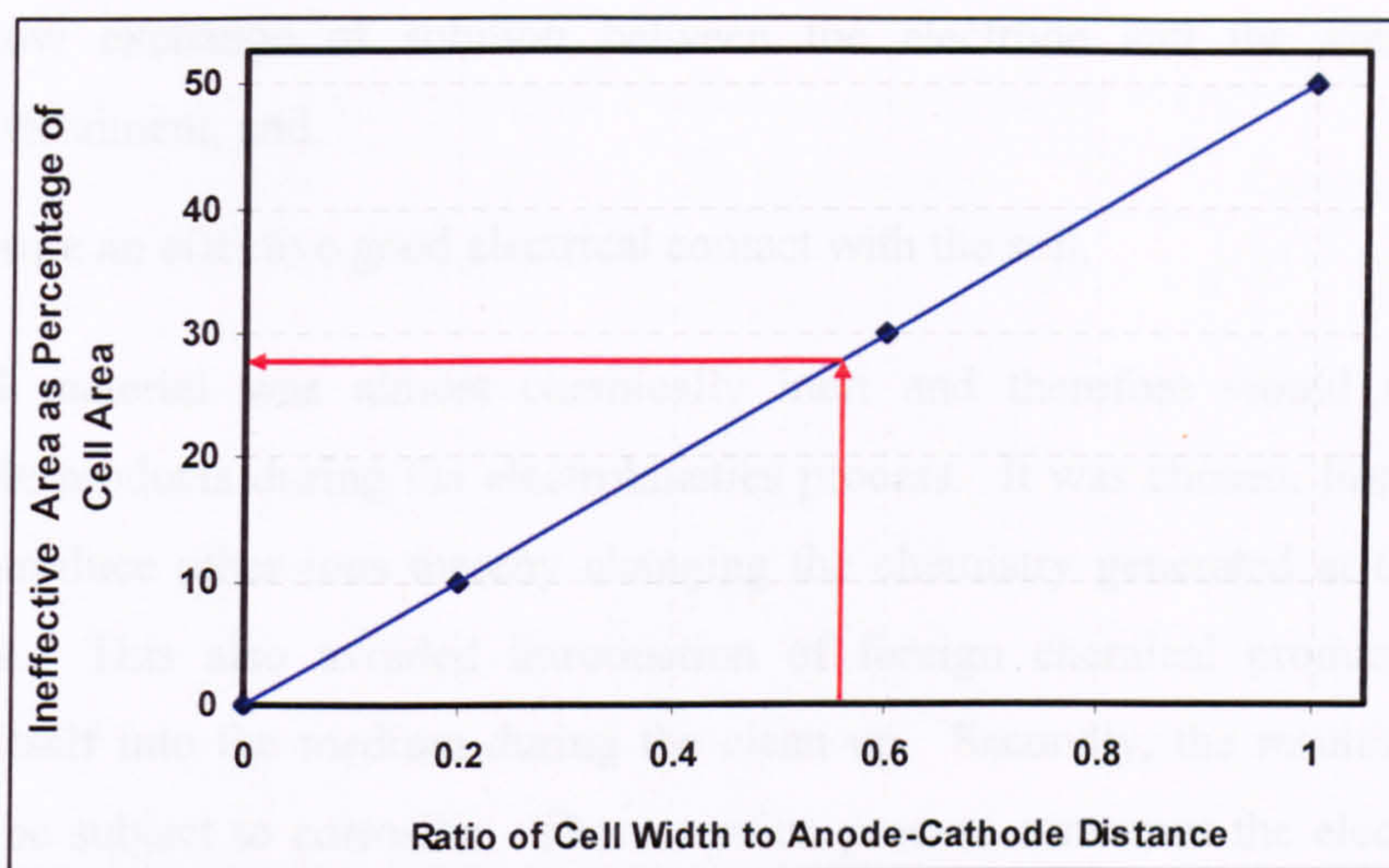


Fig 3.3 Percentage Ineffective Electric Field Areas versus Configurations of Different Width

It is illustrated in both Table 3.1 and Figure 3.3 that the percentage of inactive area for selected configurations decreases when the width of the test cell is reduced. The ultimate solution of reducing the inactive spots would involve reducing the cell widths to a minimum i.e. to the diameter of the electrodes. In field applications this is unpractical and uneconomical.

In this study, the cell length was chosen as 410mm giving a length of 360mm between the electrodes (refer to Section 4.1.5) while the cell width was chosen as 200mm. These dimensions were selected in an attempt to minimize boundary effects and presented reasonable electrode spacing between bench-scale experiments and field application. The resulting ratio of cell width to anode-cathode length was about 0.55. From Figure 3.3 this yields an inactive region of nearly a quarter of the cell i.e. 12.5% on either side of the cell. This was considered to be cost efficient for field remediation situations.

3.2.4 Electrodes

As discussed in Chapter 2, various electrodes have been used before by vendors and researchers. This study, however, sought to use the Netlon EKG electrodes (Section 2.5.5). The type selected was in form of an electrically conductive prefabricated vertical drain. Therefore, besides providing drainage, the conductivity of the core would facilitate electric current flow into the soil enabling the electrokinetics process.

This electrode configuration was essential for proper functioning of the process as it would:

- a) allow exchange of solution between the electrode and the subsurface soil environment, and
- b) ensure an effective good electrical contact with the soil.

The EKG material was almost chemically inert and therefore would not produce electrozable products during the electrokinetics process. It was chosen, firstly so that it did not introduce other ions thereby changing the chemistry generated at the electrode boundaries. This also avoided introduction of foreign chemical products from the electrode itself into the medium during the clean up. Secondly, the resulting electrode could not be subject to corrosion. The corrosion process consumes the electrode. This ensured the electrodes longevity.

3.2.5 Choice of Contaminant

Heavy Metal

According to the Environment Protection Act of 1990, there are 40 different classes of contamination in Britain. These are classified according to their risk levels by two approaches: either by physical characteristics caused by past industrial usage (e.g. gasworks) or by chemical categorisation based on generic sub-groups (e.g. heavy metals). By either classification, heavy metals are found to be one of the major causes of toxicity in the environment. The United States environment protection agency (USEPA) produced a list of over 100 organic and inorganic pollutants that constitute serious health hazards (refer to Table 3.2), fourteen of the pollutants on this priority list are metals. They are: antimony, arsenic, asbestos, beryllium, cadmium, chromium, copper, cyanide, mercury, nickel, selenium, silver, thallium and zinc. These metals are known to contribute to the larger percentage of groundwater contamination (Powell et al., 1998). Unlike organic compounds, metals are non-biodegradable (Section 1.1) and, therefore, are mainly removed from the contaminated soil, ground water or wastewater by removal methods only.

From the fourteen metals that appear on the USEPA pollutant list above, zinc metal was the one chosen for the purpose of the study since it is one of the most common heavy metal contaminant in UKs. Furthermore, because of its many uses, modern life is inconceivable without zinc (Van Assche and Martin, 2005).

Table 3.2 United States Environmental Protection Agency's List of Priority Pollutants

Base-Neutral Extractable	Acid Extractable	Pesticides
Acenaphthene	p-Chloro-m-cresol	Aldrin
Acenaphthylene	2-Chlorophenol	a,b, g, or d BHC
Anthracene	2,4-Dichlorophenol	Chlordane
Benzidine	2,4-Dimethylphenol	4,4'-DDD
Benzo(a)anthracene	4,6-Dinitro-o-cresol	4,4'-DDE
Benzo(b)fluoranthene	2,4-Dinitrophenol	4,4'-DDT
Benzo(k)fluoranthene	2-Nitrophenol	Dieldrin
Benzo(ghi)perylene	4-Nitrophenol	a Endosulfan
Benzo(a)pyrene	Pentachlorophenol	b Endosulfan
Bis(2-chloroethoxy)methane	Phenol	Endosulfan sulfate
Bis(2-chloroethyl)ether	2,4,6-Trichlorophenol	Endrin
Bis(2-chloroisopropyl)ether	Total phenols	Endrin aldehyde
Bis(2-ethylhexyl)phthalate	Volatiles	Heptachlor
4-Bromophenyl phenyl ether	Acrolein	Heptachlor epoxide
Butyl benzyl phthalate	Acrylonitrile	Inorganics
2-Chloronaphthalene	Benzene	Antimony
4-Chlorophenyl phenyl ether	Bis(chloromethyl) ether	Arsenic
Chrysene	Bromodichloromethane	Asbestos
Dibenzo(a,b) anthracene	Bromoform	Beryllium
Di-n-butyl phthalate	Bromomethane	Cadmium
1,2-Dichlorobenzene	Carbon tetrachloride	Chromium
1,3-Dichlorobenzene	Chlorobenzene	Copper
1,4 Dichlorobenzene	Chloroethane	Cyanide
3,3'-Dichlorobenzidine	2-Chloroethyl vinyl ether	Mercury
Diethyl phthalate	Chloroform	Nickel
Dimethyl phthalate	Chloromethane	Selenium
2,4-Dinitrotoluene	Dibromochloromethane	Silver
2,6-Dinitrotoluene	Dichlorodifluoromethane	Thallium
Di-n-octyl phthalate	1,1-Dichloroethane	Zinc
Fluoranthene	1,2-Dichloroethane	
Fluorene	1,1-Dichloroethylene	
Hexachlorobenzene	trans-1,2-Dichloroethylene	
Hexachlorobutadiene	1,2-Dichloropropane	
Hexachlorocyclopentadiene	cis-1,3 Dichloropropene	
Hexachloroethane	trans-1,3-Dichloropropene	
Indeno(1,2,3-c,d) pyrene	Ethylbenzene	
Isophorone	Methylene chloride	
Napthalene	1,1,2,2-Tetrachloroethane	
Nitrobenzene	1,1,2,2-Tetrachloroethene	
N-Nitrosodimethylamine	Toluene	
N-Nitrosodiphenylamine	1,1,1,-Trichloroethane	
N-Nitroso-din-propylamine	Trichloroethylene	
Phenathrene	Trichlorofluoromethane	
Pyrene	Vinyl chloride	
Polychlorinated biphenyl's		
Toxaphene		
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1,2,4-Trichlorobenzene	

According to Paterson et al., (2003), zinc is a major soil contaminant in both rural and urban areas, and is found to exist at numerous industrial sites throughout the UK. Analysis of 725 Scottish soils (Berrow and Reaves, 1986) showed presence of zinc at several places in Scotland with concentration levels ranging between 0.7 and 987 mg/kg and a mean concentration of 58 mg/kg.

Kelly et al. (1996) carried out work which compared heavy metal concentrations in two urban areas of Britain - the London Borough of Kingston-upon-Thames and Wolverhampton in the West Midlands. In Richmond, higher concentrations of heavy metals (mainly lead and zinc) were found in developed areas compared to open space. While in Wolverhampton, levels of zinc were particularly high in areas of historical and contemporary industrial activity.

Paterson et al. (2003) also referred to a study they made in 1996 which looked at the concentration of heavy metals in the topsoils in and around Aberdeen in Scotland. Results showed that even for that city with relatively little industrial activity urban soils showed significant increases in a range of metals, principally zinc, lead, copper and barium.

Clay (1995) reported that it was believed that food grown in the UK may be contaminated through the common practice of using sewage sludge, often laden with heavy metals, as a fertilizer for edible crops. She revealed in her report, soil quality studies had shown traces of zinc, copper, cadmium, nickel, and chromium on such farmlands.

Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH. At higher pH, zinc can form carbonate and hydroxide complexes which control its solubility. It readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations (Smith et al., 1995). Sorption to sediments or suspended solids, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increases as pH increases and salinity decreases.

Zinc is commonly used to coat iron and other metals for prevention of oxidation. The metal is also used among many applications in pesticides, chemical/petroleum processing, construction/demolition, electrical/electronic manufacturing, industrial waste disposal wells, machine shops, photo processing/printing, synthetic / plastics production, etc.

Various zinc salts are also used industrially in wood preservatives, accelerators for rubber vulcanization, ceramics, textiles, fertilizers, pigments and batteries (USDHHS, 1993).

Zinc metal is harmful if swallowed or inhaled. It causes irritation to skin, eyes, and respiratory tract. It is water reactive and may affect the gum tissue, central nervous system, kidneys, blood and reproductive system. The clinical signs of zinc toxicosis include: vomiting, diarrhoea, red urine, icterus (yellow mucous membranes), liver failure, kidney failure, anaemia.

Despite the prevalence of zinc in soil, most previous studies on heavy metal electrokinetic remediation of soils appear to have focused on other heavy metals such as lead, cadmium and copper (Thompson, 1989; Hamed, 1990; Hamed et al., 1991; Pamukcu and Wittle, 1992; Wittle and Pamukcu, 1993; Acar et al., 1994; West and Stewart, 1995; Acar and Alshawabkeh, 1996; Sah and Chen, 1998). Very few studies have been reported on the removal of zinc by electrokinetic remediation. Only two laboratory investigations were reported to evaluate the electrokinetic removal of zinc; Lageman, (1989) where the type of electrodes used were not reported and Alshawabkeh et al. (1997) where the removal of zinc was hindered by the presence of high calcium concentration.

Zinc chloride was selected as a source of zinc in aqueous solution ($\text{Zn}^{2+}(\text{aq})$) because zinc does not occur naturally in elemental form, (Smith et al., 1995). Secondly, although zinc chloride is corrosive and causes burns to any area of contact, and is harmful if swallowed or inhaled, it was considered less toxic than its cousin heavy metals compounds (ILO, 2002). Thirdly, studies conducted by Gardner (2005) on chlorides showed that they are effectively removed by electrokinetics from all sections of treated specimens by simply being evolved as chloride gas from the anode according to the following reaction:



Zinc itself is classified in ICRCL 59/83 as phytotoxic, that is, it is not normally hazardous to human health. As such, it was bound to pose less of a health risk to the investigator than other listed heavy metal contaminants such as cadmium and mercury.

Contamination Concentration

Previous studies showed that, despite the low flow rates, the highest degree of metal cation transport occurred in specimens whose initial contamination levels were highest, (Section 2.4.1). Increasing ionic concentration increases the electrical conductivity (implying that the electrical resistance reduces) of the specimen. For constant current and decontamination rate, the power consumption is given by:

$$Power = (Current)^2 \times (Resistance) \quad 3.1$$

Therefore, it is proportional to the resistance, which reduces as the concentration of mobile ions increases. The energy efficiency of electromigration will therefore increase with increasing metal contamination concentration.

Specifically, according to work by West and Stewart (1995) and others, electrokinetic metal decontamination is more effective (in terms of percentage contaminant reduction) at contaminant concentrations above the cation exchange capacity (CEC). When the metal concentration is above the CEC, a significant proportion of the contaminants are not sorbed to the clay (Section 2.3.2.4). Therefore, they are easily moved by electromigration, and will start to migrate immediately on voltage application.

At initial levels of metal contamination below the CEC, metal removal efficiencies are lower since they are limited by the rate of desorption from the clay (Section 2.3.2.4). Complete decontamination, requires full metal desorption from the clay (especially if the contaminant is sorbed onto the clay).

For the technology to be adequately proven, it was considered necessary to be able to extract heavy metals from contaminated soils at concentrations both below and above the CEC of the soil. Since it had already been established that the removal efficiencies were better at metal levels higher than CEC, it was deemed necessary to investigate the performance of the technology with clay specimens contaminated at concentrations much lower than the CEC. This study looked at concentrations which were in the region of 5% of the CEC of the soil. The detailed concentration calculations are presented in Section A.1 in the appendix.

Kaolin possesses a low CEC of approximately 3 me/100g. The zinc concentration on the kaolin solid phase required to satisfy this CEC, was calculated and found to be approximately 98 mg/100g of kaolin, taking into account that zinc ions are divalent (Section A.1). Classically, the CEC was assumed that it was going to originate from zinc cations being specifically adsorbed at permanently charged sites on the clay surface, these charged sites resulting from isomorphous substitution of Al^{3+} for Si^{4+} in the lattice.

3.2.6 Choice of Voltage

From the literature review, it was observed that most researchers operated between the voltage gradient of 0.1 and 1 V/cm. It was apparent that increased applied voltage gradient causes an increase in metal cation mobility towards the cathode, resulting in higher removal efficiency of the metal contaminant. However, at high voltage gradients, high current densities are induced which also increase the rate at which H^+ and OH^- ions are generated due to electrolysis reactions. The rate at which the soil can allow these ions to migrate through it is limited and hence the removal efficiency does not increase proportionally to the rate at which electrolysis reactions occur (Reddy and Shirani 1997). Therefore operating at lower voltage gradients may be more efficient for the process. West and Stewart (1995), working with lead and kaolin, indicated that voltages greater than 0.75V/cm led to excessive gas build-up in the porous stones used in their experiments as electrodes. The excessive gas build up increased the cell resistivity thereby hindering the metal extraction. In this study therefore, a lower voltage gradient of 0.5 V/cm was deemed appropriate and consequently selected for all the tests. Since the distance (i.e. centre to centre) between electrodes used in this study was 36cm, a voltage of 18V was necessary to produce the required gradient of 0.5 V/cm.

RESEARCH MATERIALS AND METHODOLOGY

4.0 Introduction

This chapter begins with a detailed description of the major materials and apparatus adopted in the research, followed by the experimental procedures. Tests described only looked at zinc metal removal from the specified soil samples. A summary of all tests conducted is presented at the end of the chapter.

4.1 Research Materials and Apparatus

4.1.1 Clay Soil

The clay soil used in all the experiments was kaolin. Kaolin was selected because it was a soft, pure, extremely fine, earth-y mineral which was very easy to work with. It was consistent and easily controllable i.e. identical samples could be produced if prepared the same way. It was also chosen because kaolinite, the main component if kaolin, is commonly a major constituent of natural soils in the UK. Additionally, many other researchers had worked with the same material making it possible to compare results.

In its natural state, kaolin is a white powder consisting principally of the hydrous aluminium silicate clay mineral kaolinite, which, under the electron microscope, is seen to consist of roughly hexagonal, platy crystals ranging in size from about 0.1 micrometer to 10 micrometers or even larger. These crystals may take vermicular and book like forms and occasionally macroscopic forms approaching millimetre size are found. Figure 4.1 shows the kaolinite structure depicted as a layer of silica rings joined to a layer of alumina octahedra through shared oxygens (Ciullo and Robinson, 2003).

Kaolin occurs naturally as hydrated alumino-silicate which has been fractioned and purified. It is formed by the breakdown of alumino-silicate rocks through the agency of physical and chemical influences over long periods of geological time.

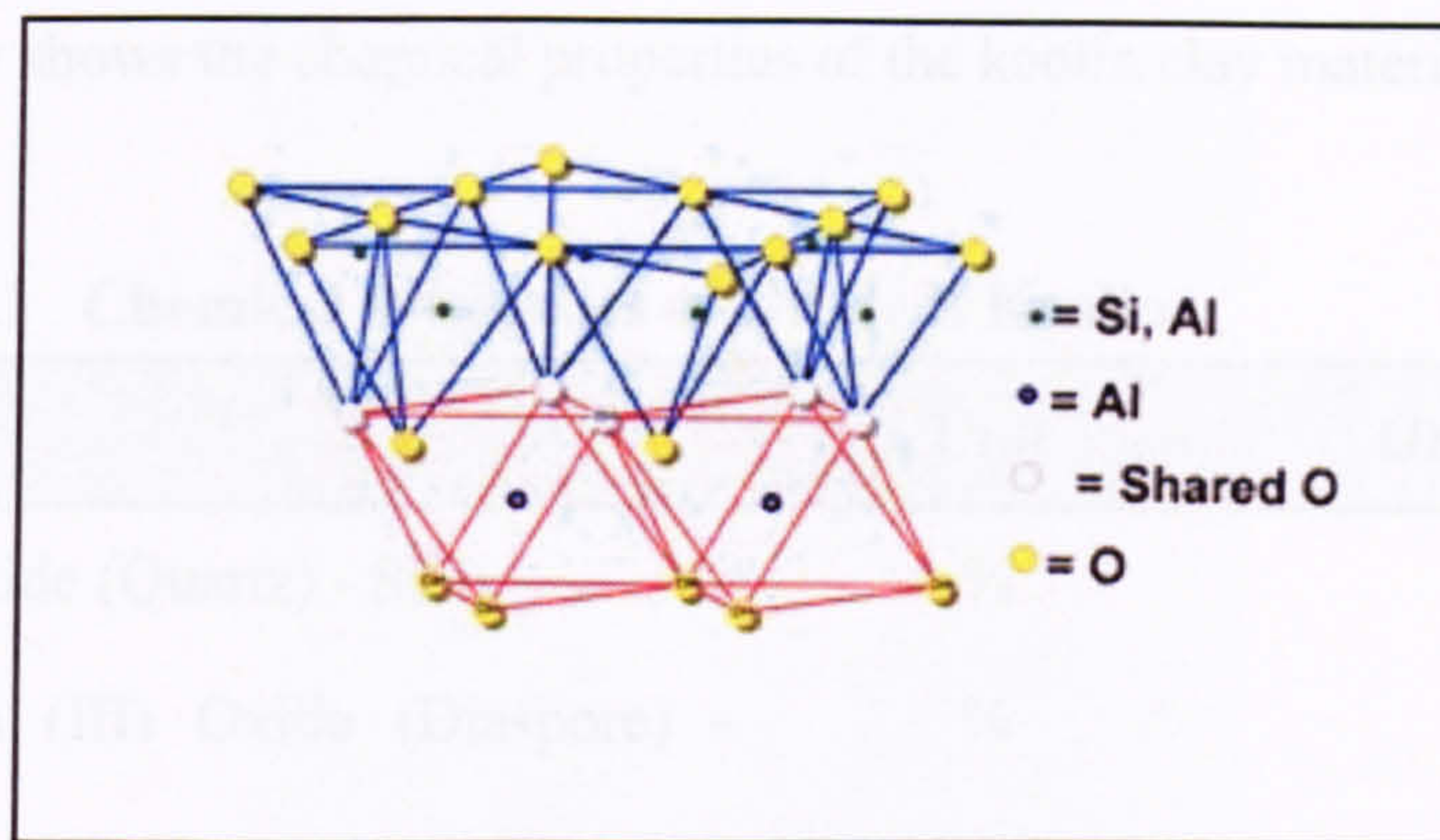


Fig 4.1 Kaolinite Structure, (Adapted from Ciullo and Robinson 2003)

The type of kaolin clay material used in the research was a white Grade E powder. It was selected since it had more uniform physical and chemical clay properties. The Grade E kaolin used for all the experiments had a Specific Gravity of 2.63 and a Specific Surface Area of 8 m²/g. The liquid and plastic limits, determined according to BS 1377-2: 1990, were 57% and 15 % respectively. The soil permeability, obtained using the falling head method, was 3.0×10^{-9} m/s. The material was a high quality medium particle size china clay produced from deposits in Cornwall (United Kingdom) and supplied by Imerys Minerals Ltd, John Keay House, St Austell, PL25 4DJ, Cornwall, (United Kingdom). The particle size distribution characteristics (refer to Figure 4.2), determined according to BS 1377-2 1990, showed that the material was a well graded very fine clay.

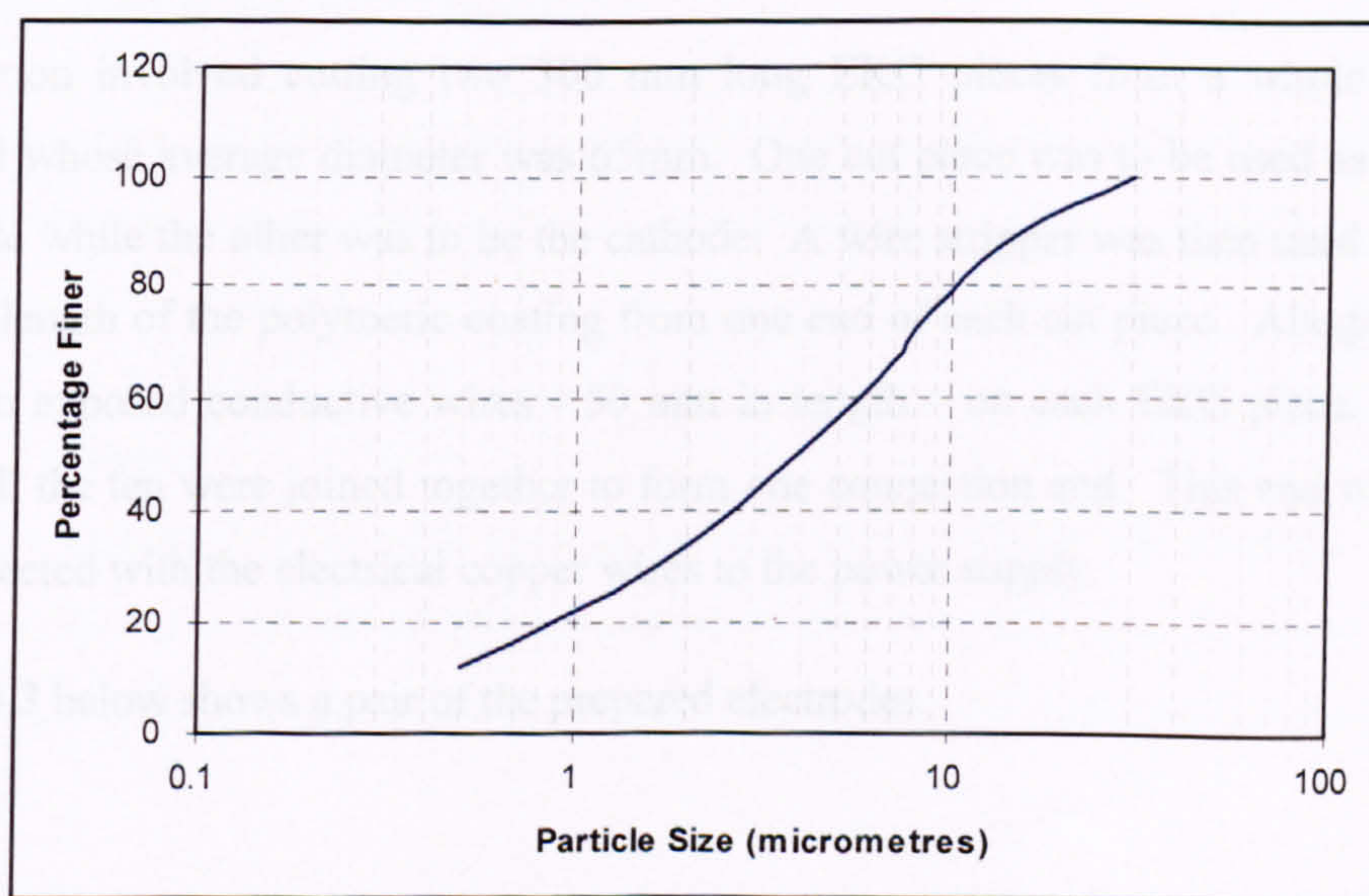


Fig 4.2 Particle Size Distribution Graph for Grade E Kaolin

Table 4.1 below shows the chemical properties of the kaolin clay material used.

Table 4.1 Chemical Properties of Grade E Kaolin*

Property	Unit	Grade E
Silicon Oxide (Quartz) - SiO_2	%	50
Aluminium (III) Oxide (Diaspore) - Al_2O_3	%	35
Alkalis (K_2O , Na_2O)	%	2.7
Iron (III) Oxide - Fe_2O_3	%	1.1
Loss on Ignition	%	11.0
Water-Soluble Salt Content	%	0.15
pH at 10% Solids		5.0 ± 0.5
Water Content Maximum	% Max	1.5

* Values given in the manufacturer's manual

4.1.2 Electrodes

The Netlon EKGs, shown in Figure 4.3, were used for both anode and cathode electrodes (refer to Section 2.5.5).

Preparation involved cutting two 300 mm long EKG pieces from a whole length of material whose average diameter was 65mm. One cut piece was to be used as the anode electrode while the other was to be the cathode. A wire stripper was then used to remove 50 mm length of the polymeric coating from one end of each cut piece. Altogether there were ten exposed conductive wires - 50 mm in length – on each EKG piece. For each piece, all the ten were joined together to form one connection end. This end was later to be connected with the electrical copper wires to the power supply.

Figure 4.3 below shows a pair of the prepared electrodes.

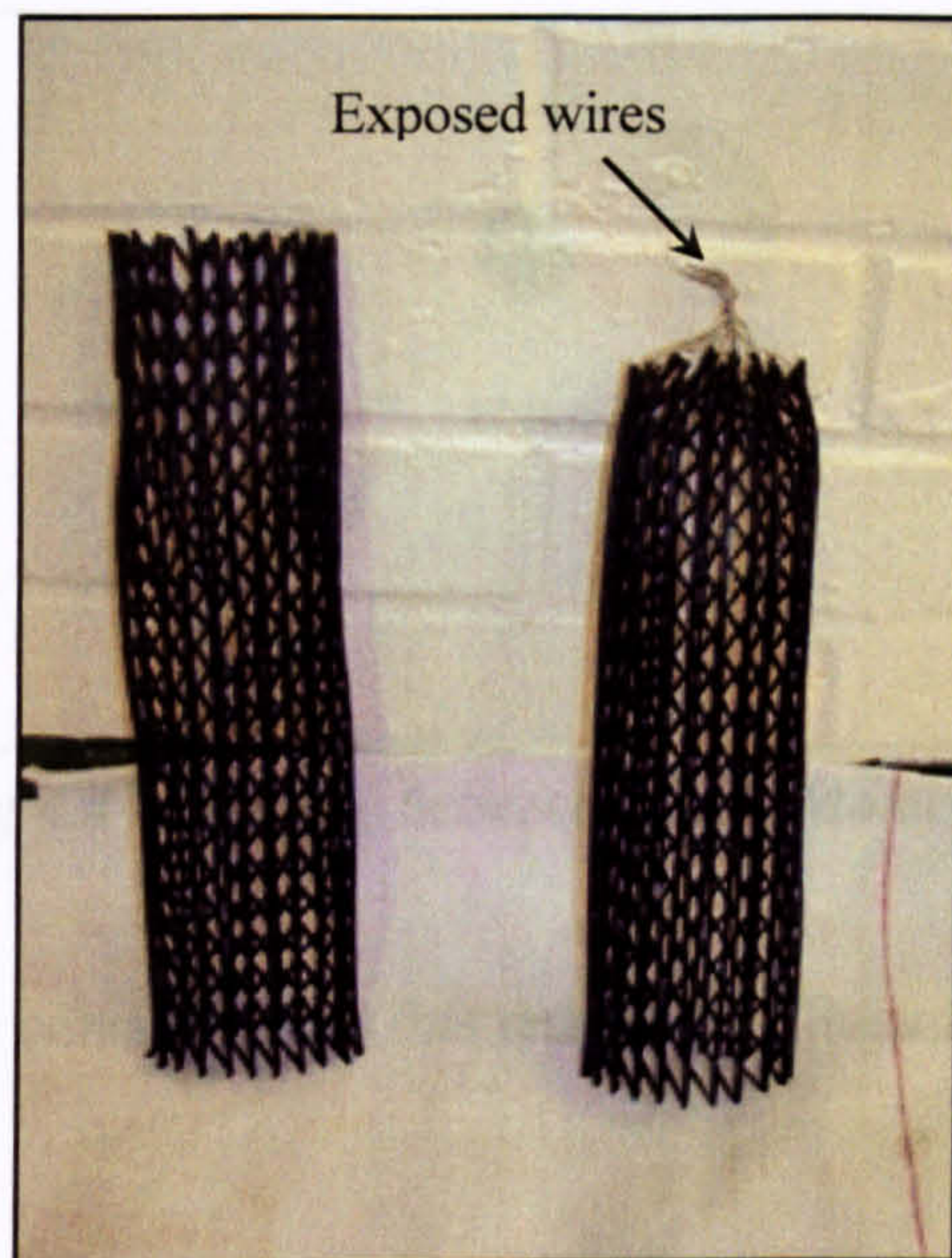


Fig 4.3 *Pair of Netlon Electrokinetic Geosynthetic*

4.1.3 Contaminant

Solid anhydrous zinc chloride (ZnCl_2) was used as the contaminant (refer to Section 3.2.5). It exists as white hygroscopic crystalline odourless granules and has a molecular weight of 136.3 g. Its boiling and melting points are 732°C and 290°C respectively. It has a density of 2.9 g/cm^3 and solubility of 432 g/100ml of water at 25°C . Zinc chloride has very good solubility in water where it dissociates into Zn^{2+} and Cl^- ions as follows:



Zn usually occurs in the 2+ oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zn may precipitate as $\text{Zn}(\text{OH})_{2(\text{s})}$, $\text{ZnCO}_{3(\text{s})}$, $\text{ZnS}(\text{s})$, or $\text{Zn}(\text{CN})_{2(\text{s})}$.

4.1.4 Solvent

The main solvent worked with throughout was water. Water has a simple molecular structure. It is composed of one oxygen atom and two hydrogen atoms as shown in Figure 4.4. Each hydrogen atom is covalently bonded to the oxygen via a shared pair of electrons.

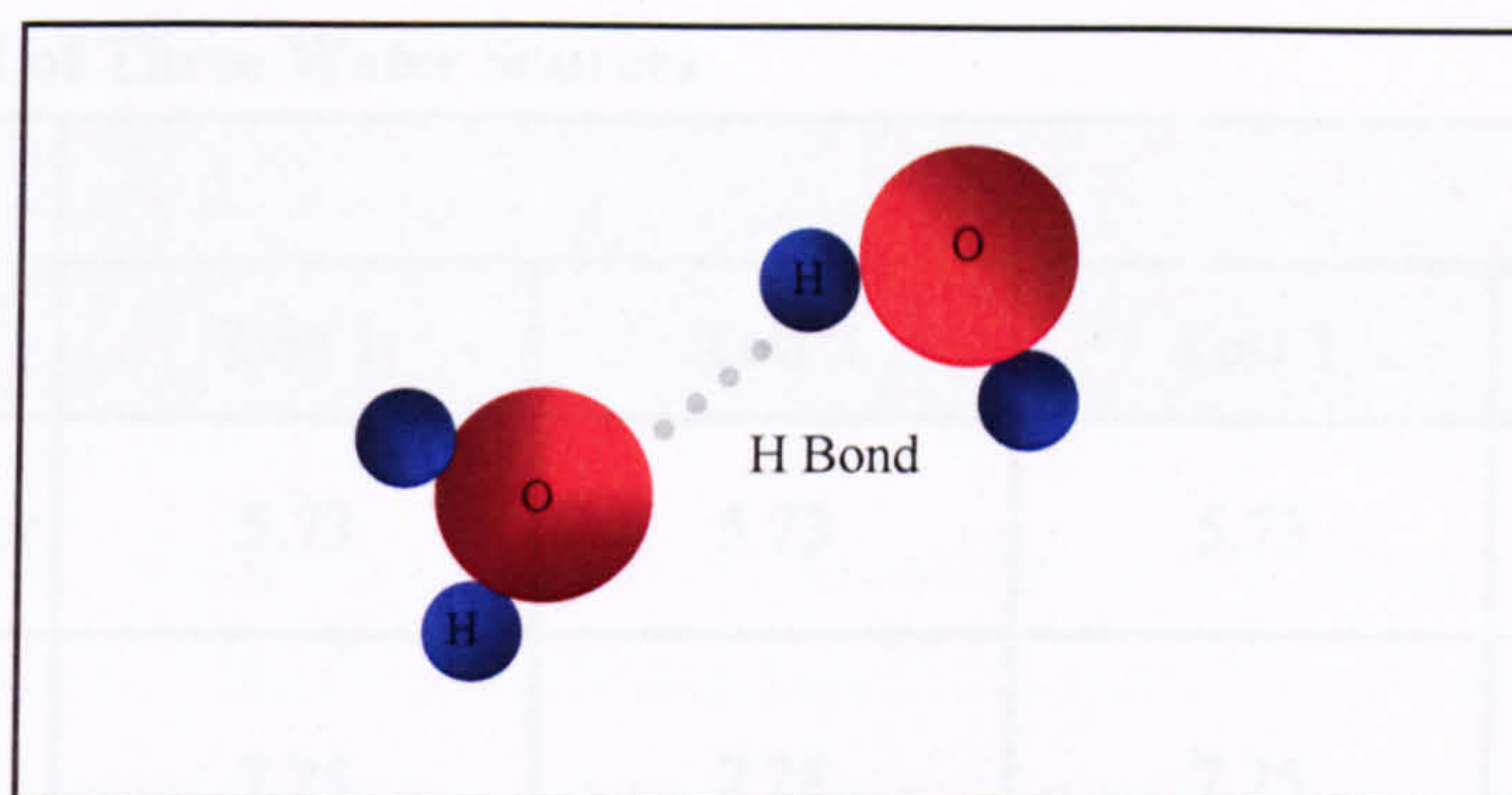


Fig 4.4 Bonding between Water Molecules

Three water sources were considered for this research as illustrated in the Tables 4.2, 4.3 and 4.4 below.

Table 4.2 Anion Concentration of Three Water Sources

Water Quality	Anion Concentration in mg/l						
	Fl ⁻	Cl ⁻	PO ₄ ³⁻	SO ₄ ²⁻	NO ₂ ²⁻	NO ₃ ²⁻	Total
Deionised Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tap Water (Geotechnical Laboratory)	0.8	18.3	0.0	7.4	4.0	74.0	104.5
Tap Water (Environment Laboratory)	0.7	18.2	0.0	7.1	2.9	75.8	104.7

Table 4.3 Cation Concentration of Three Water Sources

Water Quality	Cation Concentration in mg/l							
	Na ⁺	K ⁺	Ca ²⁺	Fe ²⁺	Mg ²⁺	Mn ²⁺	Zn ²⁺	Sr ²⁺
Deionised Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tap Water (Geotechnical Laboratory)	13.1	2.0	42.7	<0.1	5.7	<0.1	<0.1	0.6
Tap Water (Environment Laboratory)	7.5	2.0	43.5	<0.1	5.6	<0.1	<0.1	0.6

Table 4.4 pH of Three Water Sources

Laboratory Water Source	pH			
	Test 1	Test 2	Test 3	Average
Deionised Water	5.73	5.73	5.73	5.73
Tap Water (Geotechnical Laboratory)	7.25	7.25	7.25	7.25
Tap Water (Environment Laboratory)	7.38	7.40	7.39	7.39

Tables 4.2 and 4.3 show that laboratories tap water contained dissolved anions and cations with exact concentrations dependent on local conditions. Deionised water, however, was free of any trace of these. This was because all ions coming from dissolved compounds had been removed during the process of producing deionised water.

The pH values in Table 4.4 illustrate that the laboratory tap water was slightly alkaline. This was because the tap water pH had been purposely controlled by Northumbrian Water (water provider) treatment works to range between 7.5 and 8.0 in order to prevent corrosion of the pipes and fittings (Northumbrian Water, 2002). In contrast, the pH of deionised water was acidic (5.7 units). It is considered that carbon dioxide in the air dissolved in deionised water forming a weak carbonic acid (Equation 4.2).



Based on the chemical results observed in the tables above, deionised water was preferred. The absence of additional ions implied that the negative consequence of the direct interference by the dissolved compounds with the electromigration of the target Zn ions would be avoided. Additionally, the lower pH of deionised water was beneficial since low-pH environment inhibits metallic contaminants from being sorbed onto soil particle surfaces and favours the formation of soluble compounds (refer to Section 2.3.2).

The electro-conductivity of deionised water was measured as 35 $\mu\text{S}/\text{cm}$.

4.1.5 Laboratory Testing Tank

In the absence of any relevant standard methods or apparatus, as variations existed from author to author, a ‘fish tank’ model was chosen for the study. This type of configuration enabled rectangular specimens of medium size, with the top side open to the atmosphere, to be investigated. The rectangular open-to-the-surface configuration was deemed to be more representative of the field conditions than for instance the cylindrical closed cells, used by majority of researchers observed in the reviewed literature (refer also to Section 2.4.3). Secondly, the overall design of the cell, with the EKG electrodes directly installed in the test specimen, was considered to replicate potential field application more closely. Additionally, with this type of cell configuration, the temporal variation in the contaminating metal cation concentration along both the length and vertical depth of the cell could be monitored by easily taking samples at respective cell positions.

The fish tank was of a medium bench scale size and made of transparent perspex so that it did not conduct electricity. The adopted dimensions of the tank were 500 mm by 200 mm by 250 mm for the length, width and height respectively. Figure 4.5, below, the sketch of the tank not drawn to scale, while the pictures of the tank are presented in Figures 4.6 and 4.7. The length and height of the tank were chosen as the resulting sample length of 410 mm and height of 150 mm were deemed optimum size for the bench scale study. The width of the tank, however, was chosen based on computations methods by Alshawabkeh et al., (1999) and Alshawabkeh (2001) of effective and ineffective electric fields areas as discussed in Section 3.2.3.

The aim of the overall model was to allow water and chemical species to move uninterrupted across the whole soil sample. The interior of the tank was subdivided by two perforated transparent perspex sheets to form three chambers:

- ***Flushing Chamber*** - 45 mm long, primarily used to hold and control the de-ionised water. In order to maximise the soil/water contact area at the draw-in-point during electroosmosis in the Two Process Approach, water from this chamber was allowed to permeate into the soil specimen from the entire height and width of the chamber
- ***Effluent Chamber*** - 45 mm long, where the purge water was collected and removed via the outlet at the bottom of the chamber. The outlet had a tap which was kept open

when experiments were running. The water samples were collected for chemical analysis.

- **Soil Chamber** - 410 mm long, where the contaminated soil and EKG electrodes were inserted during experimentation, and

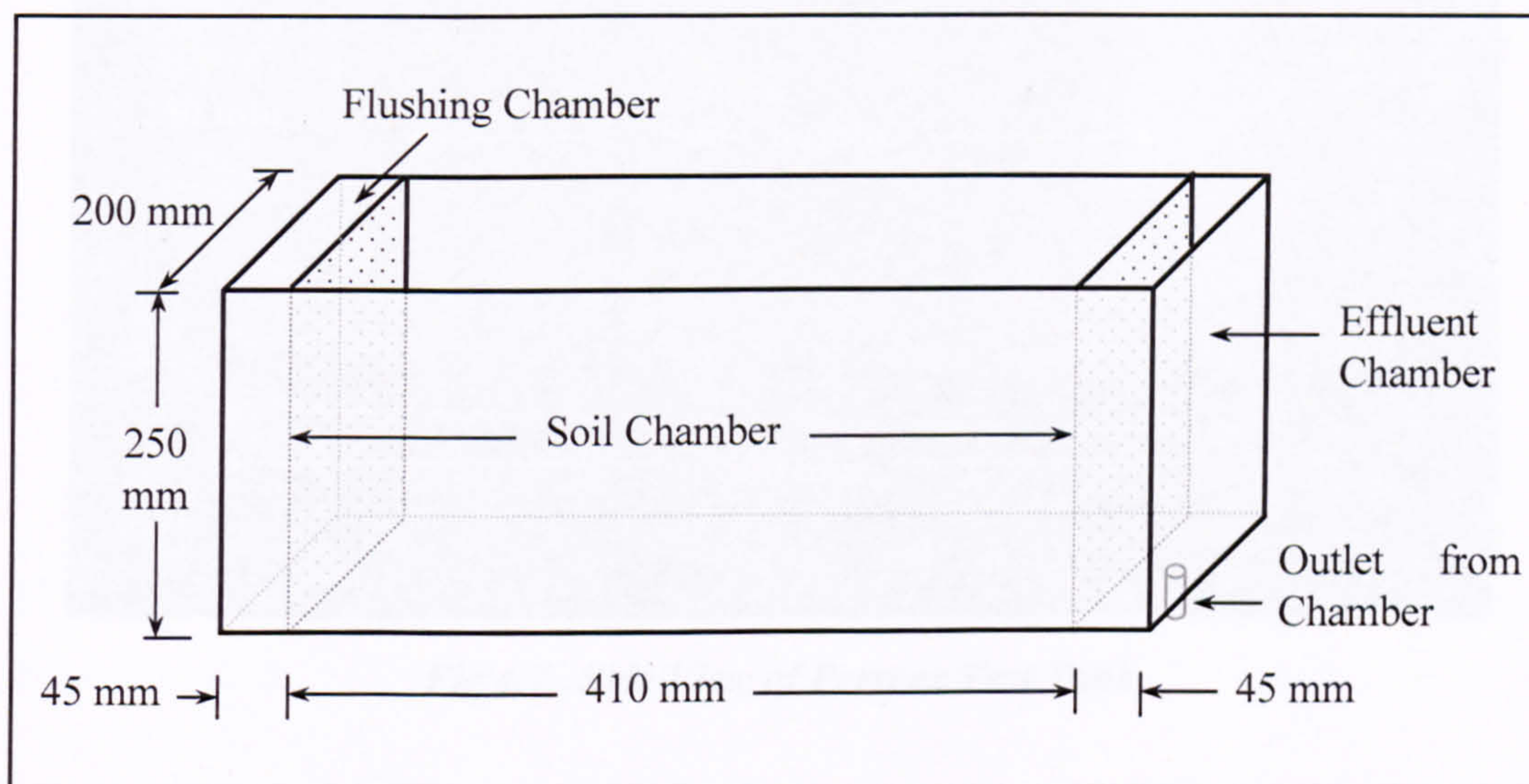


Fig 4.5 Schematic of Perspex Test Tank

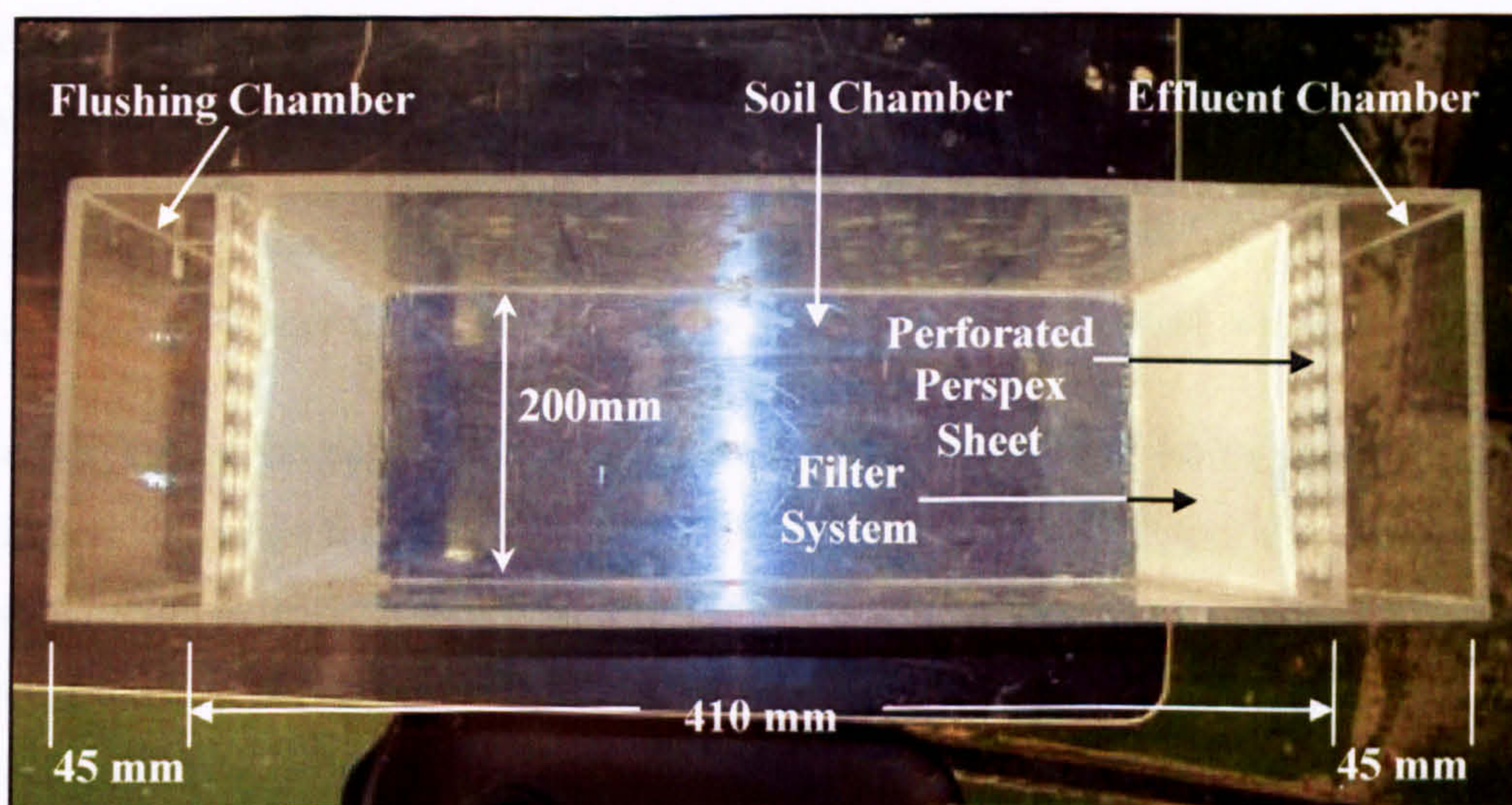


Fig 4.6 Plan View of Perspex Test Tank

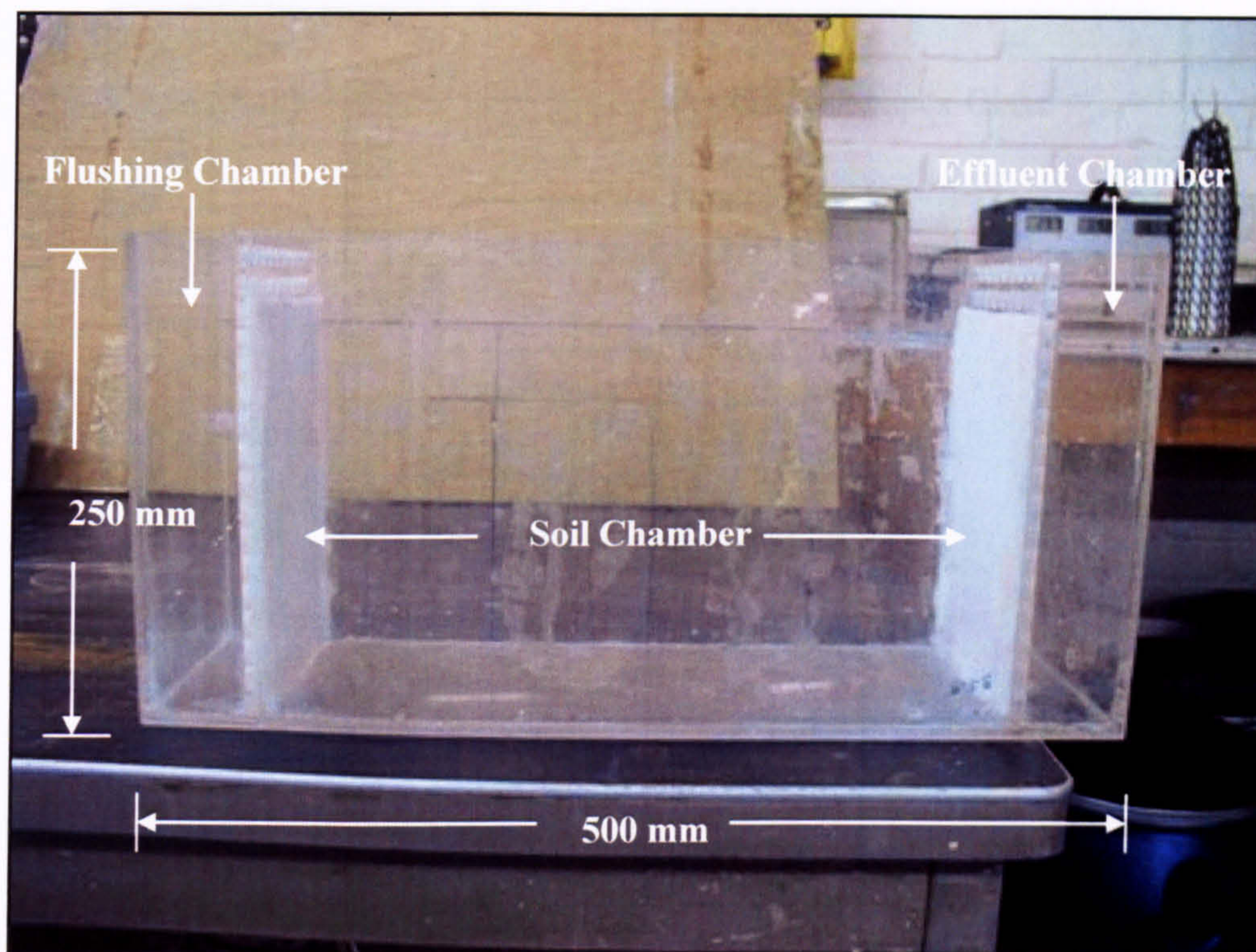


Fig 4.7 Side View of Perspex Test Tank

4.1.6 Filter System

To ensure that only water and dissolved ions were free to flow from one chamber to another, during the electrokinetic clean-up operation, a combined filter system of a geotextile and a grade 2 Whatman paper filter was used. Both were chosen for their chemical resistance to the acid and alkali environments generated by the electrode reactions.

The geotextile was a white non-woven needle-punched semi-porous fabric of 2 mm thickness. The paper filter was 0.19 mm in thickness and had particle retention of 8 μm .

The purpose of the paper filter was to prevent solid grain particles movement from the soil chamber, while the geotextile materials protected the paper filter from damage when wet. The filters, each 200 mm by 200mm in size, were glued onto the soil-side of each face of the two perforated perspex sheets thereby sandwiching the soil specimen in the soil chamber.

Figure 4.8 below shows the cross section of filters in position (drawn not to scale).

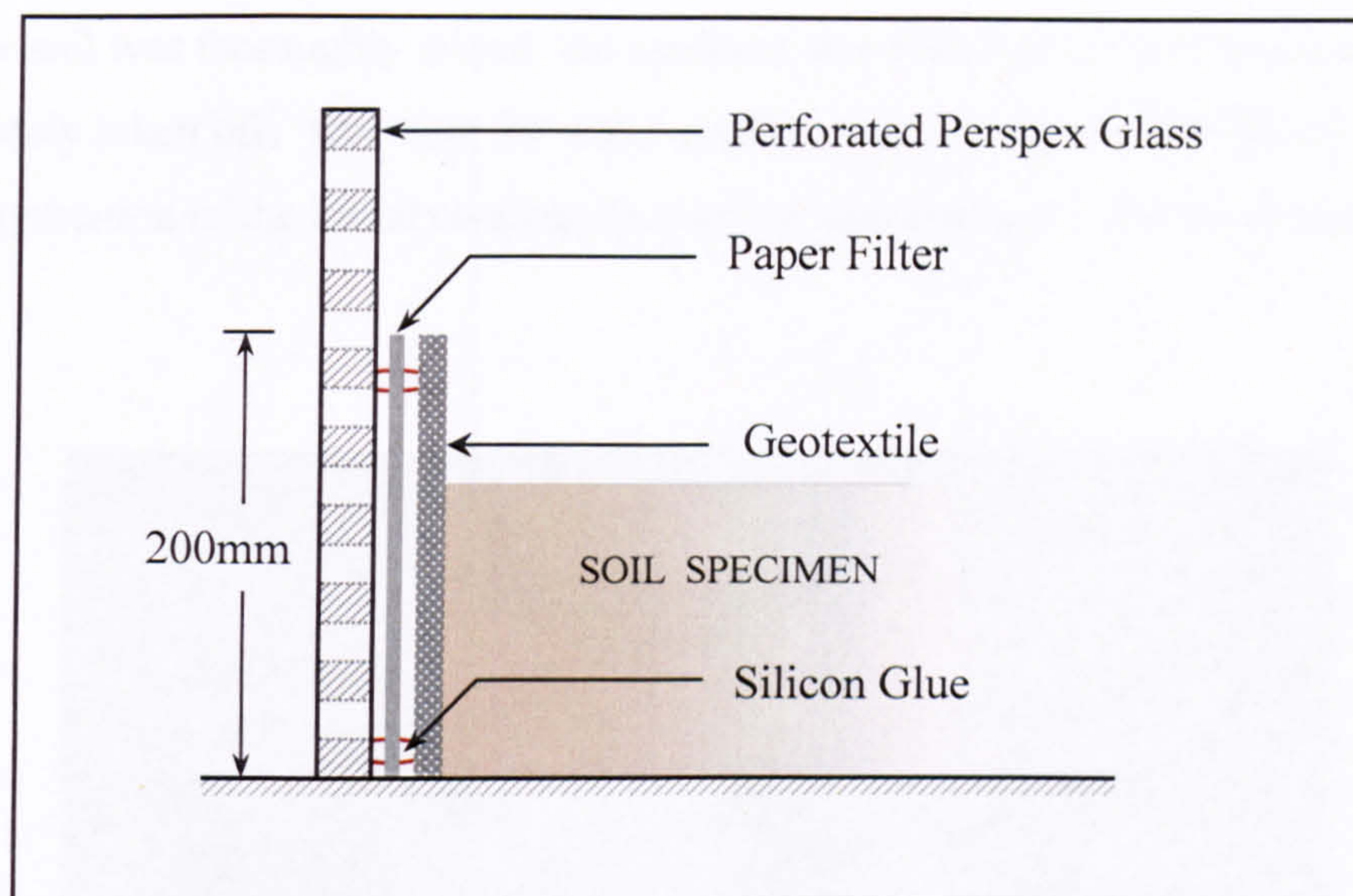


Fig 4.8 Schematic of the Filter System

4.2 Main Test Procedures

The methodology adopted during the testing programme is given in the sections below.

4.2.1 Preparation of Contaminated Sample

For each experiment, 680 mg of dry zinc chloride crystals were poured into a plastic bucket containing 6.8 litres of deionised water. Since zinc chloride is hygroscopic, the handling process of weighing and pouring it into deionised water was done as fast as possible to minimise any errors in measured masses arising from absorption of water from the atmosphere. The contaminant – water mixture was stirred, using a 25 mm long magnetic stirring element for 20 minutes, at 1400 revolutions per minute. A solution of 100 mg of zinc chloride per litre of contaminated water was formed. Longer mixing times were not deemed necessary since zinc chloride has high water solubility.

8 kg of dry kaolin Grade E clay powder was measured using a weighing scale and put into a clean industrial mixer. The zinc chloride water solution was then poured into the mixer and the mixer switched on (refer to Figure 4.9). The two were allowed to mix for at least 30 minutes forming a homogeneously contaminated soil specimen with a pH of 4.7 ± 0.1 and water content of $85 \pm 2\%$. The target water content was 1.5 times the liquid limit. At that water content, the soil sample was slurry-like, easily workable, free flowing and able to be placed into the soil chamber without creating air pockets.

Once the soil was thoroughly mixed, the machine was switched off and two samples were immediately taken off. One was for water content determination while the other was for the determination of the initial concentration of the contaminant in the specimen soil.



Fig 4.9 Mixing of Kaolin with Contaminated Water

4.2.2 Experimental Procedures

For each experiment, the contaminated soil slurry was spooned into the soil chamber of the perspex tank in small layers of about 25 mm. Each layer was carefully tamped with a clean plastic rod to remove any air trapped during the insertion process. Once the soil vertical height was 150 mm, it was levelled by lightly vibrating the tank. The outlet at the bottom of the effluent chamber was then connected to a measuring cylinder using a clean plastic tube (Figure A4.1 in appendix). The tap at the outlet was then opened.

Two EKGs were inserted directly and vertically into the soil 300cm apart but 360 mm centre to centre apart i.e. one on either side of the soil chamber (Figure 4.10), and each in the centre width (Figure 4.11). They were inserted into position by gently pushing them vertically until they reached the bottom of the cell (Figure 4.12). This configuration ensured that the electrodes filaments were in direct contact with the soil material throughout the test.

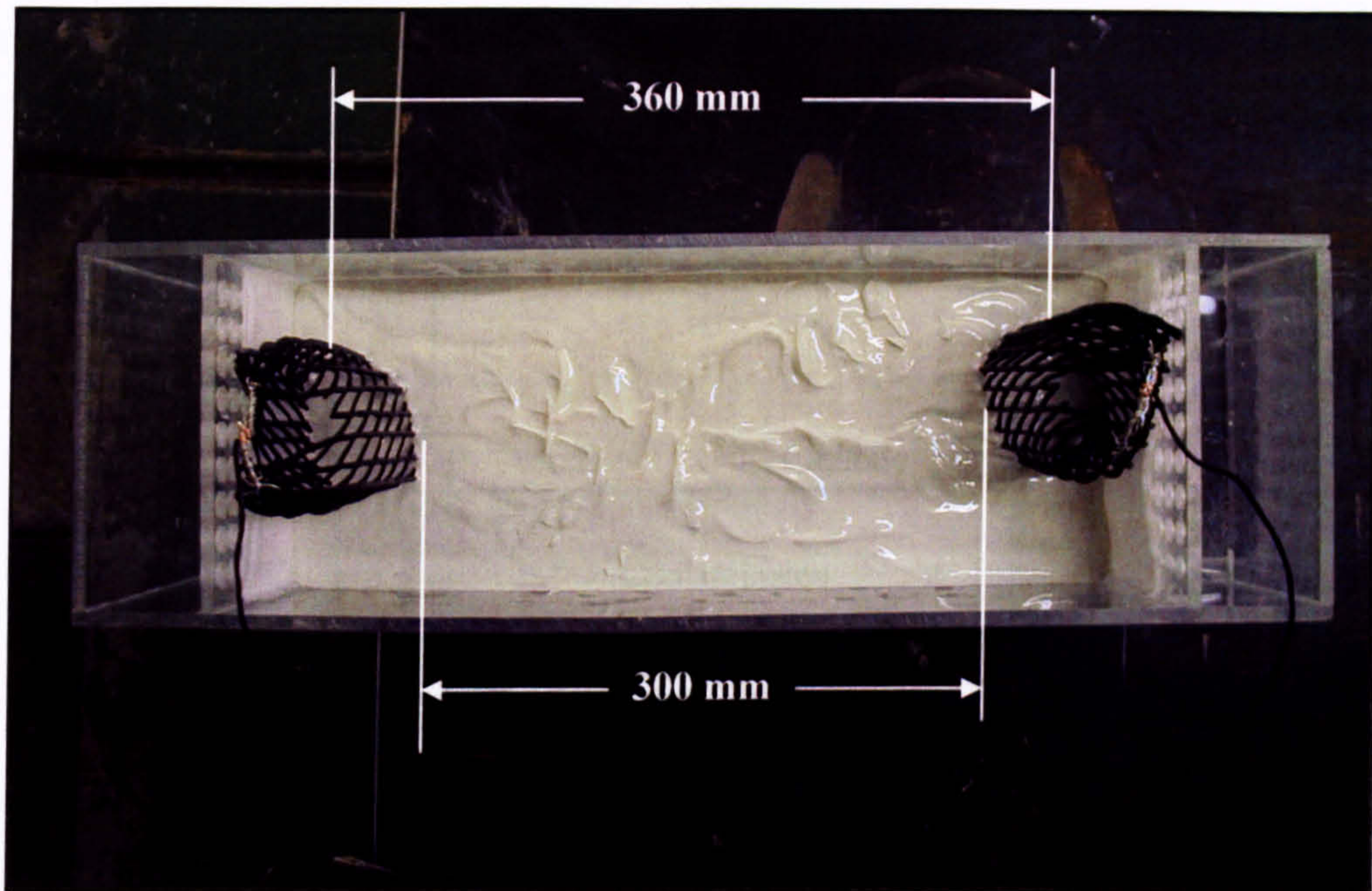


Fig 4.10 Plan View of Perspex Test Tank with Soil Specimen and EKG in Position

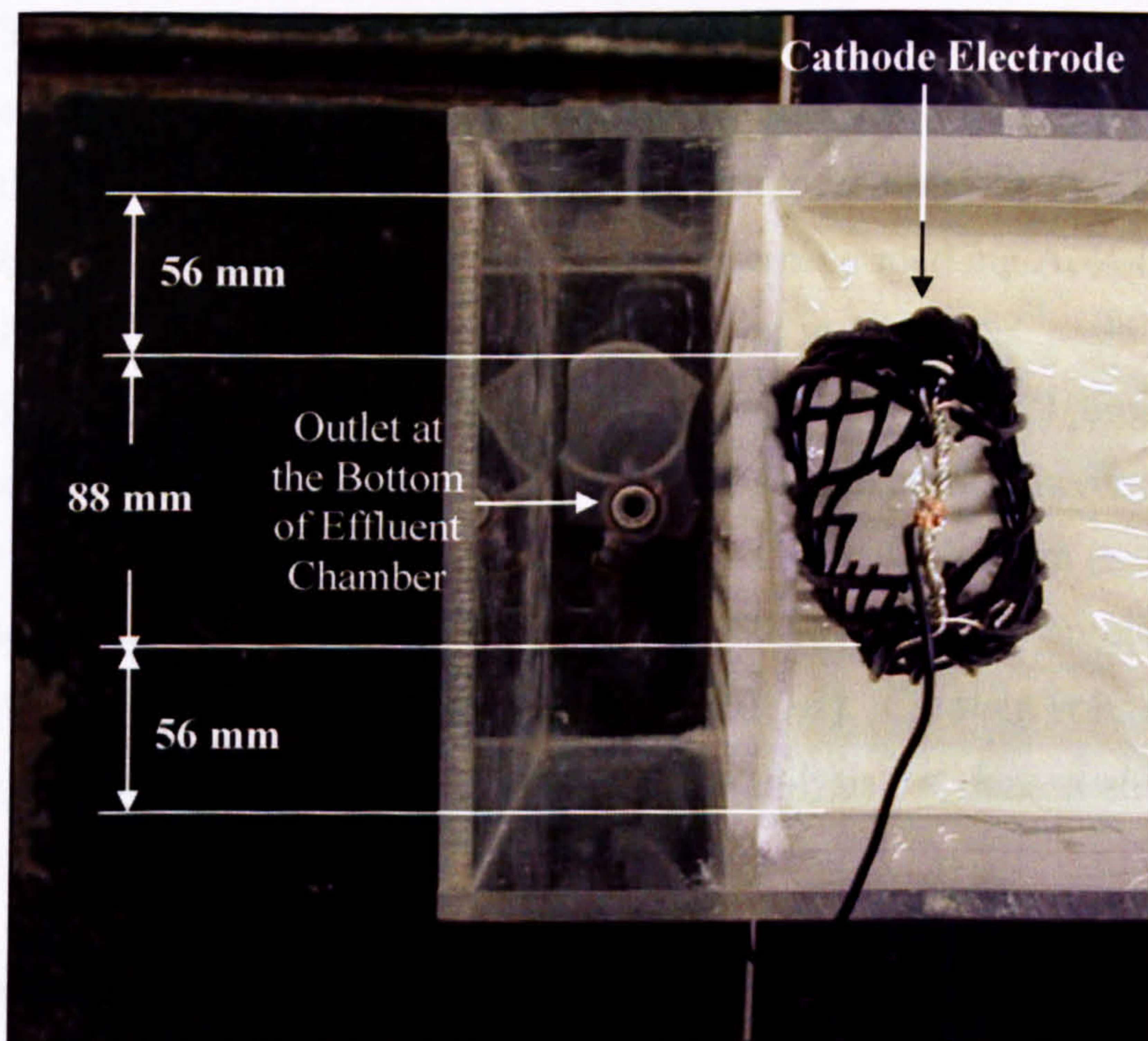


Fig 4.11 EKG Electrode Installed directly in Soil in the Centre Width of the Test Cell

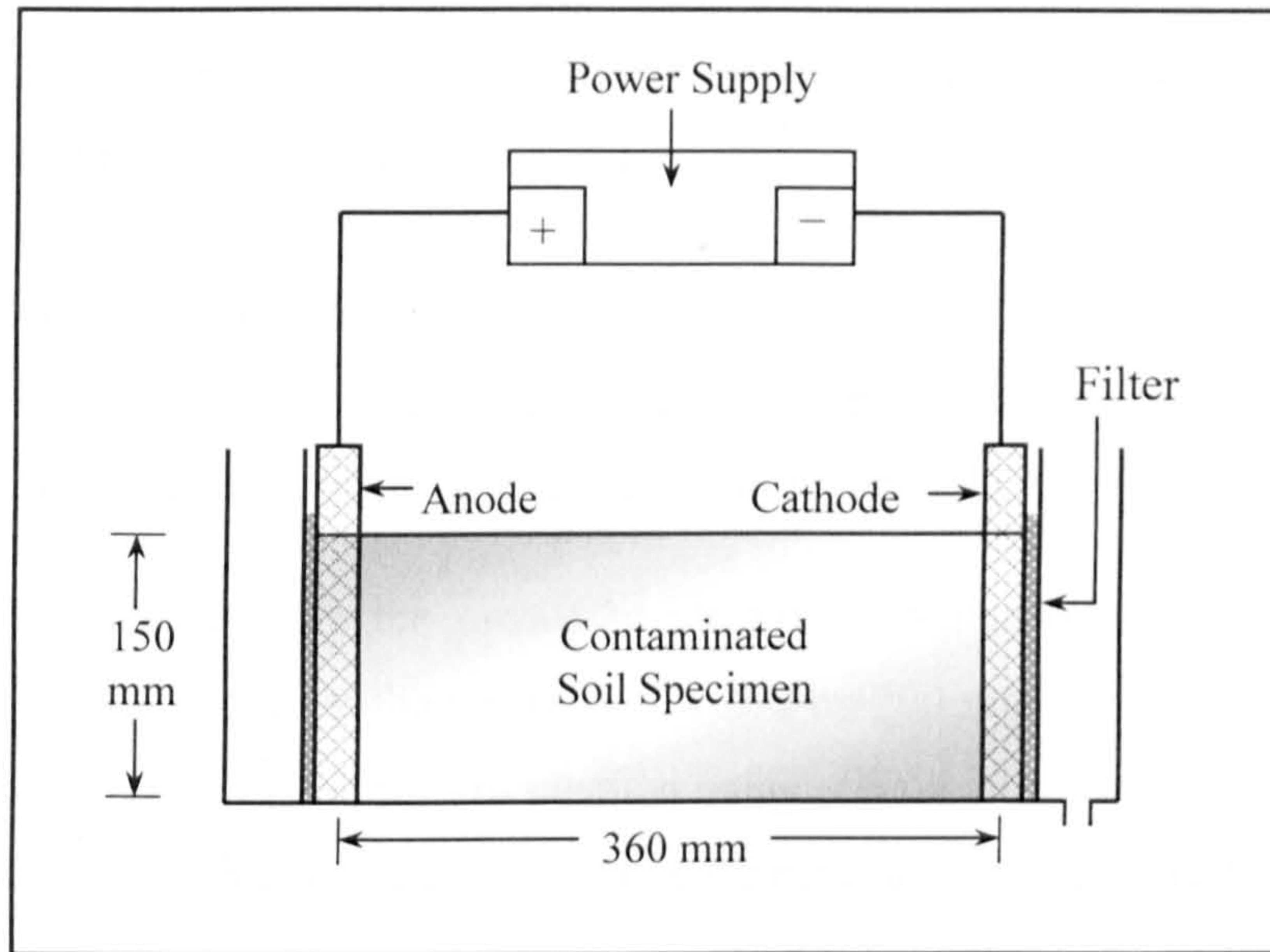


Fig 4.12 Sketch of the Experimental Set-up

The EKG on the flushing chamber side was connected to the positive (+) terminal of a Thandar TS30225 30V – 2A Precision Direct Current power supply (refer to Figure 4.13), while the one on the effluent chamber side was connected to the negative (-) terminal, consequently making them the anode and cathode electrodes respectively. The soil in the chamber was then divided into 5 key sections by externally marking A, $\frac{1}{4}$ (one quarter), $\frac{1}{2}$ (one half), $\frac{3}{4}$ (three quarters) and C onto the tank at horizontal positions from the anode. These distances were equivalent to 0, 0.25, 0.5, 0.75, and 1 times the length between the anode and the cathode respectively. The voltage of the power supply was set to 18 Volts which created a mean constant voltage gradient of 0.5 V/cm (refer to Section 3.2.6). The current switch was set to a maximum so as to achieve an electric current density in the range of 1–10 A/m² (refer to Section 2.3.3.2). Constant voltage conditions were used in all tests to keep constant net rates of electrolysis reactions at all times (Acar, et al. 1992).

Different category procedures were followed depending on the test objective. Below are the different experimental objectives with their procedures.

4.2.2.1 *Effect of Flushing Water Through the Cell*

In order to assess the effect of flushing deionised water through the contaminated soil specimen during the electrokinetic process, two experimental approaches were conducted. They are: One Process and Two Process approaches.

(a) **One Process Approach**

This experiment was operated under 'closed anode' conditions so that no deionised water was used at all in the flushing chamber as shown in Figure 4.12 and 4.13.

Tests were conducted as in the procedure already presented in Section 4.2.2 above. Instead of the filter system at the anode side, a 200 by 200 mm – 5 mm thick – perspex glass was used. This was glued into position using silicon to ensure no soil pore water seeped out of the soil chamber into the flushing chamber during experimentation.

Once the setup was complete, the power supply was switched on and the experiment deemed started. The current on the power supply was monitored over a period of time.

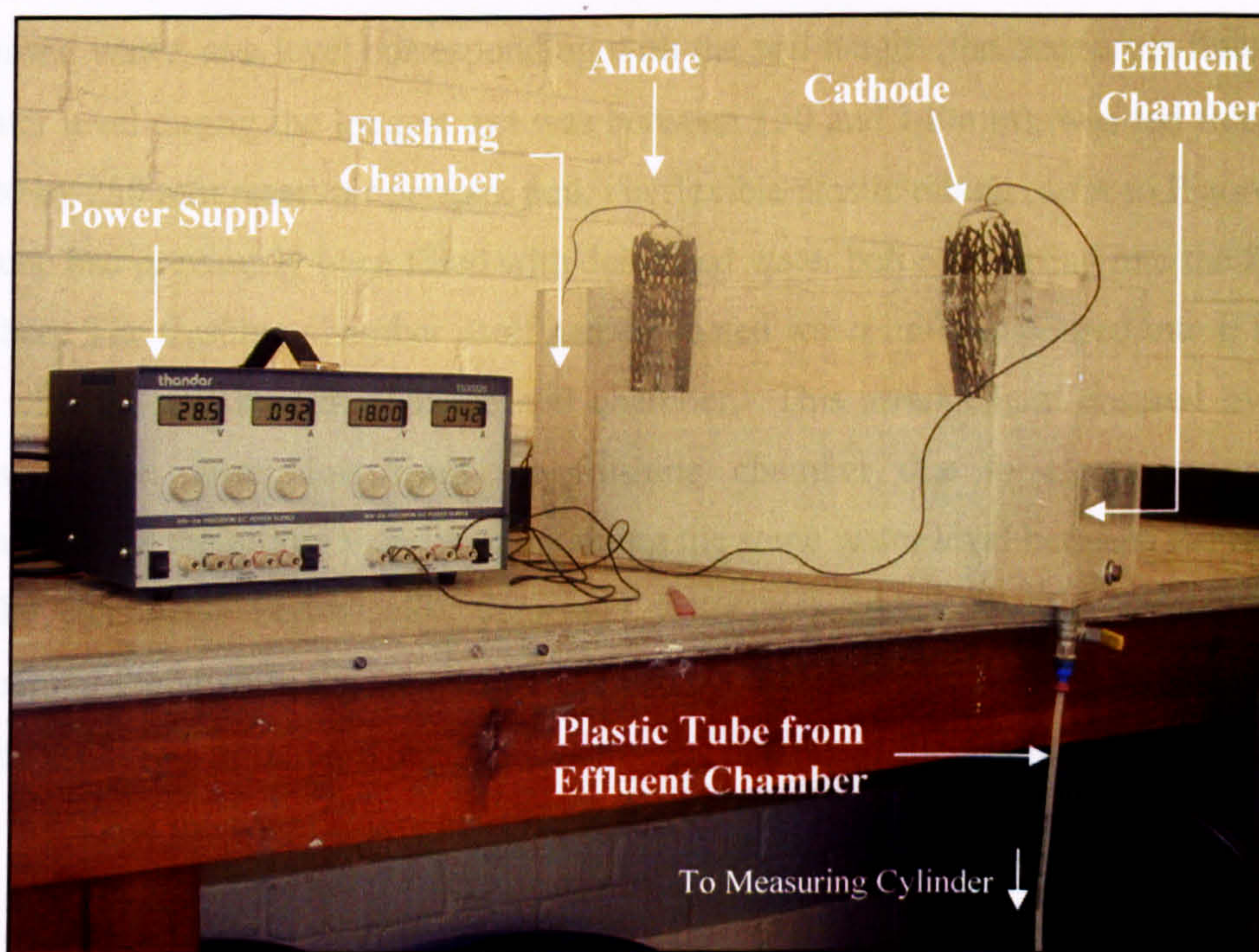


Fig 4.13 One Process Approach Experiment with no Water in the Flushing Chamber

A total of 5 bench scale tests were run. The first test was run for only 1 week, while the second was run for 2 weeks. The third, fourth and fifth were run for 3, 4 and 5 weeks respectively. Tests were run for a maximum of 5 weeks because beyond this period, the current in the cell had reduced to zero. It was considered that once the current in the cell was zero, no further electro treatment processes could occur.

At the end of the target test duration for each electrokinetic bench scale experiment above, soil samples were taken from the marked points (A, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, C) along the cell. The sampling techniques used are detailed in Section 4.2.3 later in this chapter. Samples were then taken for physical and chemical analysis (Section 4.3 and 4.4).

(b) Two Process Approach

The procedure already defined in Section 4.2.2 above was followed. Additionally, once the setup reached that stage, deionised water was added and maintained in the flushing chamber throughout the entire duration of the investigation. This water was for flushing the target ions from the 'open' anode through the contaminated soil towards the cathode when the power was turned on.

Deionised water, at a level corresponding with the soil height (the maximum fluctuations of water level during the longest test was between 150 and 140mm), was fed from a 400 by 200 by 250 mm reservoir perspex tank via flexible plastic tubing (refer to Figure 4.14). The tube had previously been filled with deionised water before inserting into the flushing chamber. The flushing chamber itself had deionised water initially poured into it to flush level with the soil specimen in the soil chamber. This arrangement ensured hydraulic continuity, i.e. water lost from the flushing chamber due to electroosmosis was replenished via the tubing thereby maintaining the same water level between the reservoir and the chamber. Periodically, deionised water was added to the reservoir thereby maintaining the level in the reservoir and flushing chamber with the soil height. This set up was preferred to using a mechanical pump because of the rapidly changing rate of water in-take at the water/soil contact surface.

Once everything was in position, and water in the chamber connected to the reservoir via the plastic tube, the experiment was started by switching the power supply on. The current on the power supply was monitored over a period of time.

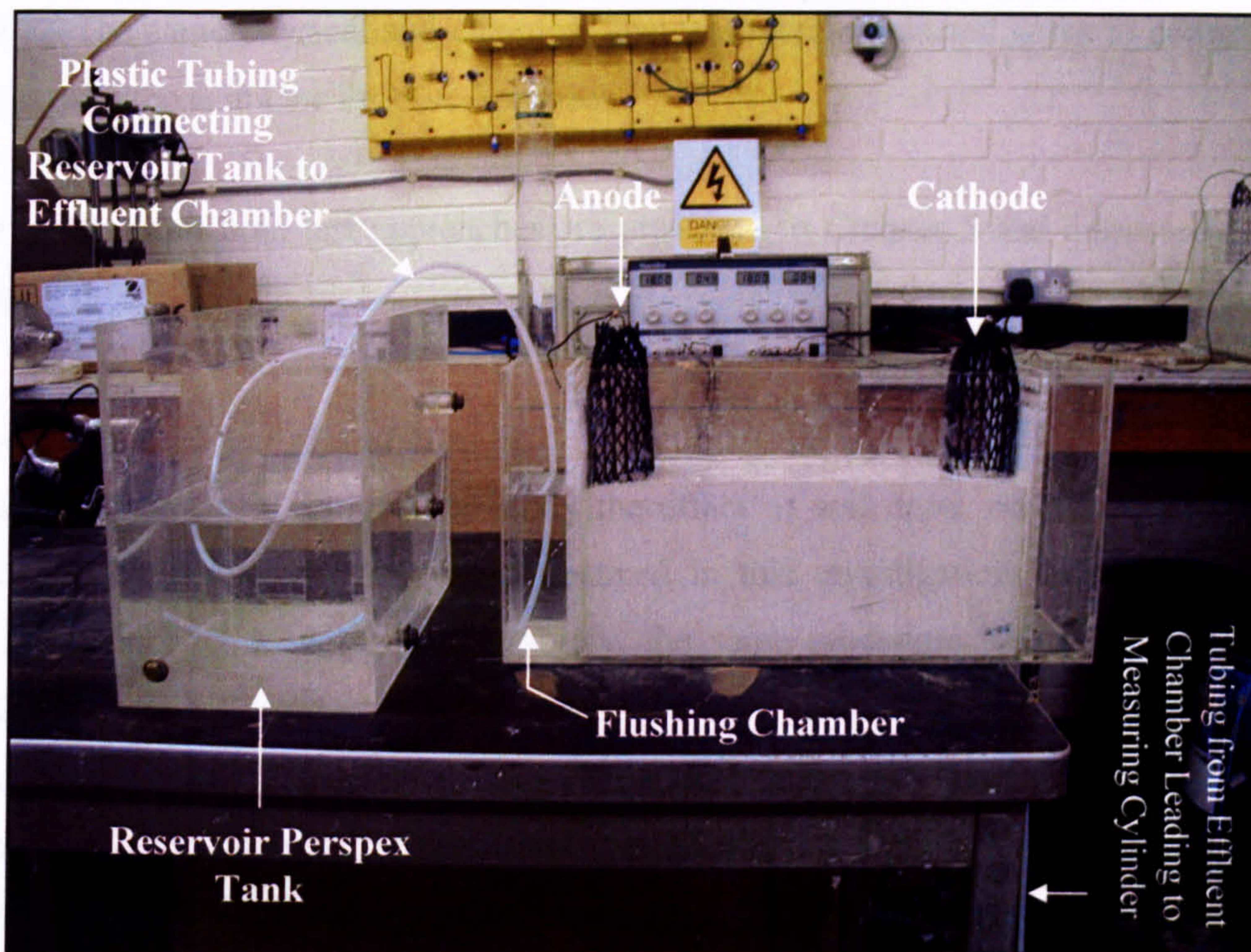


Fig 4.14 Two Process Approach Experiment with Deionised Water in the Flushing Chamber

Figure 4.15 below shows the schematic diagram of the Two Process Approach set up.

From a total of 5 bench scale tests conducted, the same amounts of specimen samples were obtained at the same specific periodicity and points as in One Process Approach

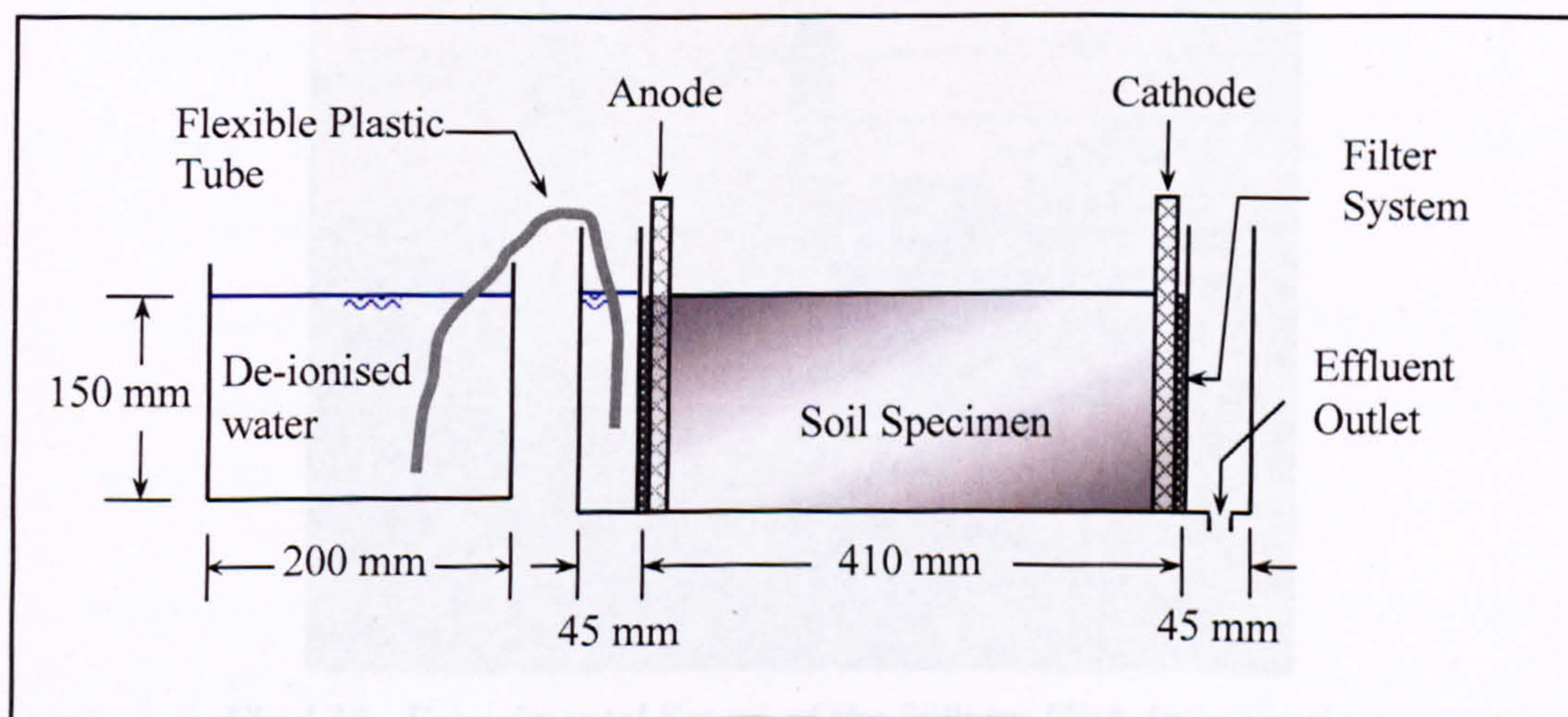


Fig 4.15 Experimental Set-up for the Two Process Approach

above. The same physical and chemical analyses were conducted so as to compare the results with those in One Process Approach.

The results from both test approaches are presented in Chapter 5 and discussed fully in Chapter 6.

4.2.2.2 Effect of Soil Height

This experiment was designed to study the effect of soil depth on the metal removal efficiency by comparing the results obtained in this investigation with those of tests conducted in Section 4.2.2.1(b). Largely, the same procedure as the one in Section 4.2.2.1(b) was followed. The difference was only in the vertical dimensions of the experimental tank, filter system, height (quantity) of the specimen material in the soil chamber and consequently the height of the deionised water in the flushing chamber. The overall horizontal dimensions for each chamber of the experimental tank remained the same.

In this instance, the heights of both the soil and deionised water in the flushing chamber, were doubled from 150 mm to 300mm (refer to Figure 4.16). Rectangular filters of 200 by 350 mm were used instead of the square ones (Figure 4.8). The rest of the set up was exactly the same as already discussed in the previous subsection.

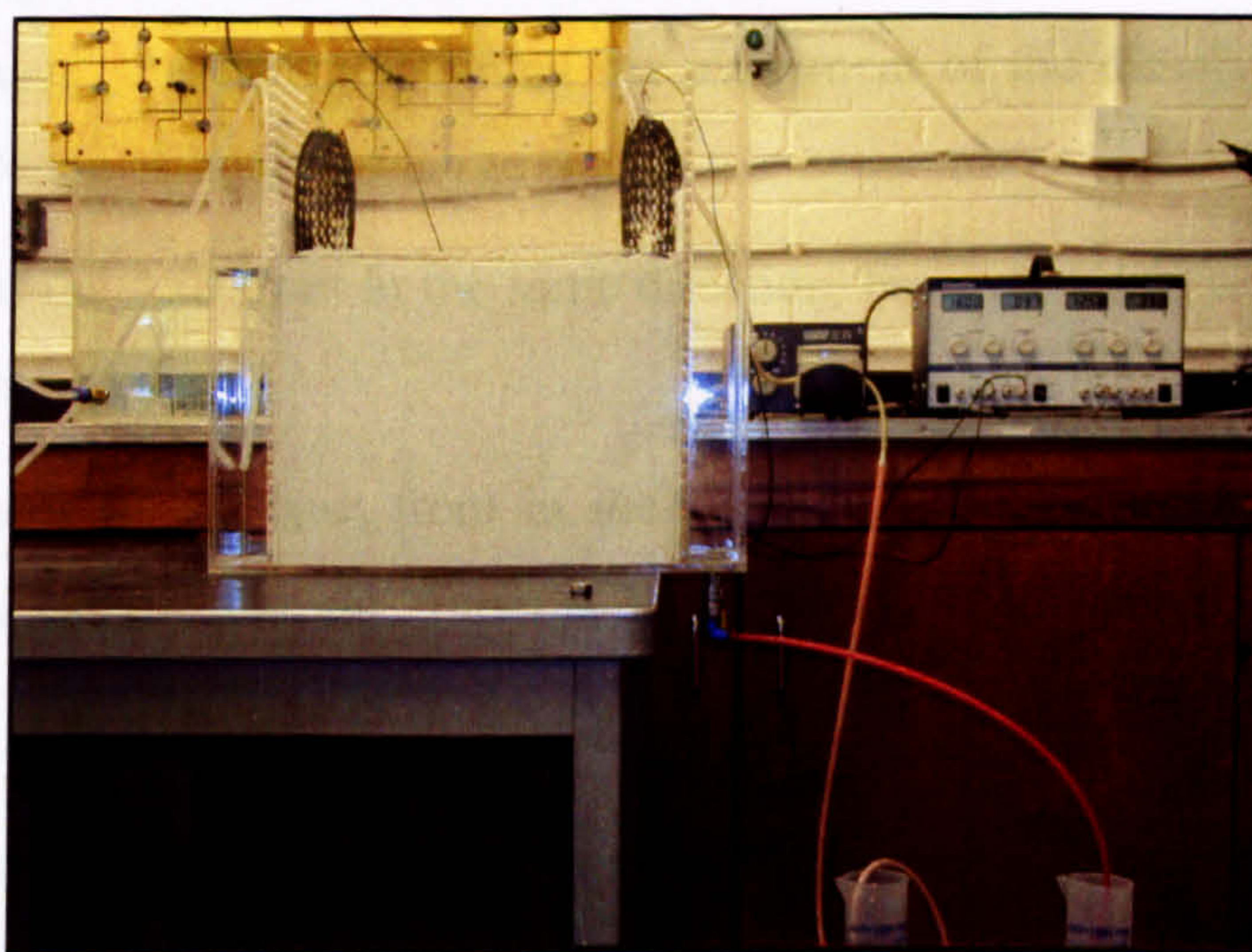


Fig 4.16 Experimental Set-up of the 300mm High Investigation

Altogether five bench scale tests were carried out with the same amounts of specimen samples being obtained at the same periodicity and sampling points as in the Two Process Approach above. The same physical and chemical analyses were conducted.

All the results are presented in Chapter 5.

4.2.2.3 *Effect of Intermittent Electrical Current*

Current intermittence is the application of a pulse voltage at predetermined on/off intervals during electrokinetic treatment. According to Micic et al. (2001), using intermittent current reduces the electrical power consumption and electrode corrosion. The results of the study conducted by Mohamedelhassan and Shang (2001) also suggested that current intermittence enhanced the electroosmotic flow, quantified as a higher coefficient of electroosmotic permeability than that conducted with a continuous direct current. Therefore, the purpose of this investigation was to determine if the benefits such as reduced power consumption (through periodic current interruption) would also result in the efficiency of treatment – in terms of metal removal - being significantly improved. It was anticipated that during the period when the current was on, the processes described in Section 2.3.2 would take place. However, once the power was turned off, it was expected that the electrokinetic processes would stop almost instantly. It was considered that during this off interval the:

- (a) seepage of pore water in the anode - cathode direction would continue due to the hydraulic head, thereby maintaining the movement of the dissolved charged metal ions towards the cathode discharge well,
- (b) migration of the acid front in the same direction, however slow, would continue due to (a) above, and that
- (c) the movement of the base front in the opposite direction would be non existent without the electric current consequently reducing premature precipitation of the metal ions.

In this investigation, the same apparatus and procedure as the one presented in Section 4.2.2.1(b) was essentially followed. However, in order to investigate the effect of the

current intermittence, the current intermittence intervals of 24 hours on and 24 hours off were used.

In operation, once the soil cell set-up was complete and in position, the current was switched on using an on/off switch. This was to allow the electrokinetic processes to proceed in the cell. After 24 hours, the electrical power was switched off. The supply remained off for 24 hours when it was switched on again for 24 hours. And so on.

For this investigation, a total of 4 bench scale tests were run. The first, second and third test durations were 1, 2 and 3 weeks respectively. The fourth test was run for up to 10 weeks. This period was selected by doubling the maximum time the last experiment in Two Process Approach was allowed to run. This was based on the fact that the actual time this cell was run with the electrical current was equivalent to 5 weeks as was the case in the specimens treated with continuous direct current.

As in the previous tests above, at the end of the test for each electrokinetic bench scale experiment, soil specimen samples were retrieved at specific points along the cell. These were taken for physical and chemical analysis.

The results are given in Chapter 5.

4.2.2.4 Monitoring pH along the Cell

In order to study the variation of pH in the pore water during the electroosmotic process, a special drainage geotextile, 25mm thick, was used to create a drainage channel which consequently trapped a water medium between the soil mass during the electrokinetic process. This type of geosynthetic had a plastic drainage area between two 1mm thick non-woven geotextiles on either side.

Using silicon glue, they were fixed in the soil chamber at the a quarter ($\frac{1}{4}$), mid cell ($\frac{1}{2}$) and three quarter ($\frac{3}{4}$) distances from the anode consequently subdividing this chamber into 4 equal compartments approximately 90 mm long (Figure 4.17). Contaminated soil, prepared as already explained in Section 4.2.1, was then placed and carefully compacted in the resulting four compartments to the height of 150mm. The compaction was to remove any air trapped.

Two EKGs were vertically inserted (by slowly pushing them till the bottom) into the first and last soil compartments i.e. one on either side of the soil chamber. The EKG on the flushing chamber side was connected to the positive (+) terminal of the power supply, while the one on the effluent chamber side was connected to the negative (-) terminal. Deionised water was added to a height of 150mm and maintained in the flushing chamber during the entire period of the experiment. Water contaminated at the same level as the one used in the specimen soil mixture, i.e. 100 mg of zinc chloride per litre of de-ionised water, was then poured into the three drainage channels to a height of 150mm. The voltage in the power supply was set to 18 Volts which was equal to a voltage gradient of 0.5V/cm. The power supply was then switched on.

The total experiment duration was 5 weeks during which about 5ml of liquid samples were periodically retrieved from each of the 5 positions i.e. at the anode, cathode as well as the 3 cavities defined above. Using a hand held 6P CAMLAB ultrameter (refer to Figure A.2 in the appendix), the pH of each collected sample was measured as soon as it was collected.

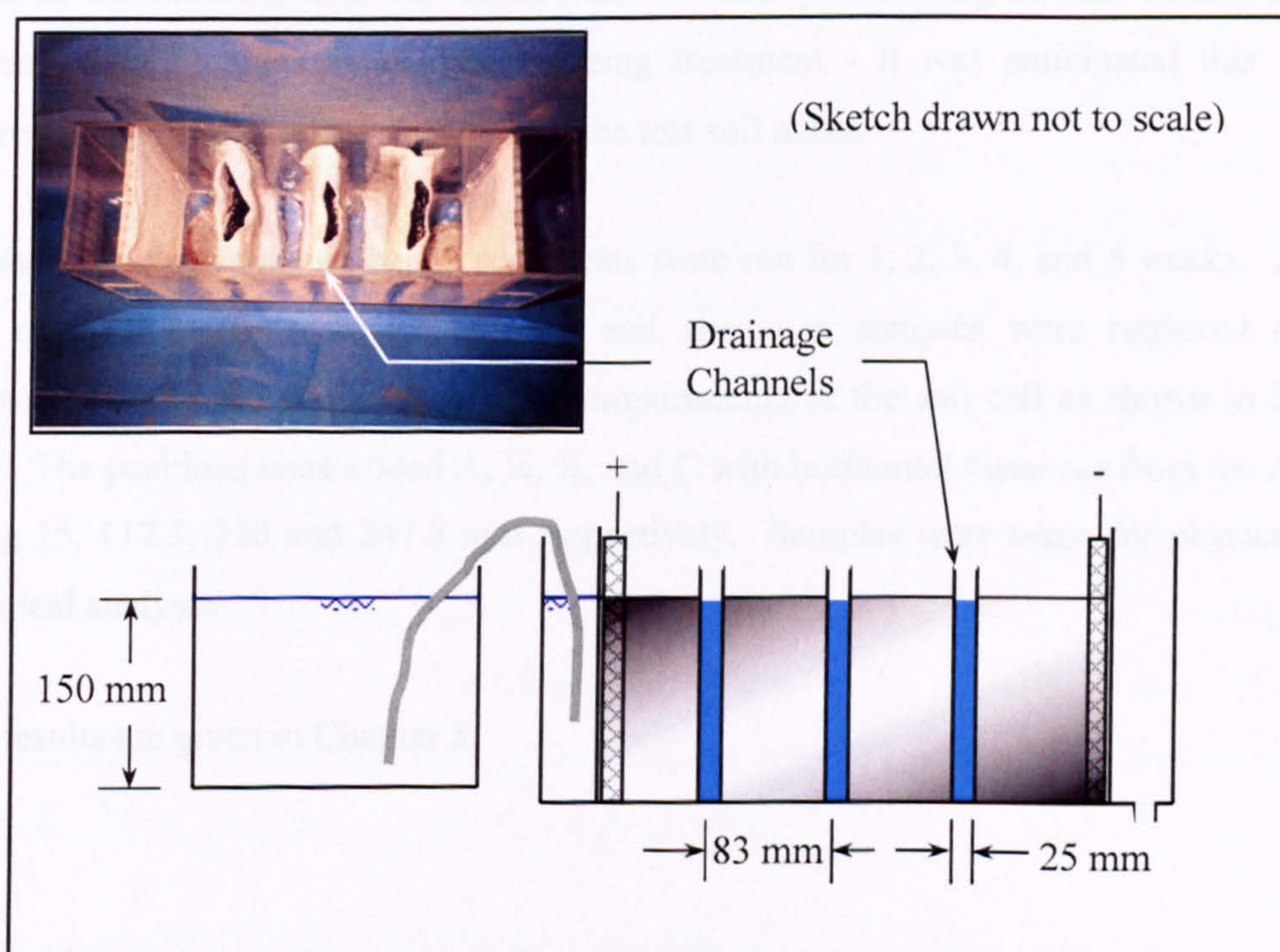


Fig 4.17 Experimental Set up with Partitionings (Inset shows a Picture of the Channels Already Glued in Position)

In this investigation only Two Process Approach tests were run. The pH for the One Process Approach could not be investigated using the drainage channel method. This was because the pore water in the unflushed soil specimen was not sufficient to be trapped in the channels set up along the sample lengths. In an unirrigated anode environment the samples began drying up in just under one week of electrokinetic operation.

4.2.2.5 Effect of Changing Water in the Drainage Channels

In this investigation, the whole procedure as presented in Section 4.2.2.4 was followed. The only difference was that deionised water was used in the drainage channels instead of contaminated water.

Once the experiment was started, by applying a constant voltage gradient of 0.5 V/cm across the test specimen, the drainage channel waters were replenished with fresh deionised water every after 24 hours. This was done by pumping out the polluted water from each channel, and as fast as possible replacing it with fresh clean deionised water to flush level with the soil in the cell. Therefore, by periodically replacing the polluted water in the channels with the 'clean water' - thereby increasing the soil surface area in contact with uncontaminated water during treatment - it was anticipated this would improve the removal of the metals from the test soil mass.

A total of 5 electrokinetic bench scale tests were run for 1, 2, 3, 4, and 5 weeks. At the end of each bench scale experiment, soil specimen samples were retrieved at the horizontal mid point of each of the 4 compartments of the soil cell as shown in Figure 4.18. The positions were coded A, $\frac{1}{4}$, $\frac{3}{4}$, and C with horizontal distances from the Anode being 15, 117.5, 220 and 247.5 mm respectively. Samples were taken for physical and chemical analysis.

The results are given in Chapter 5.

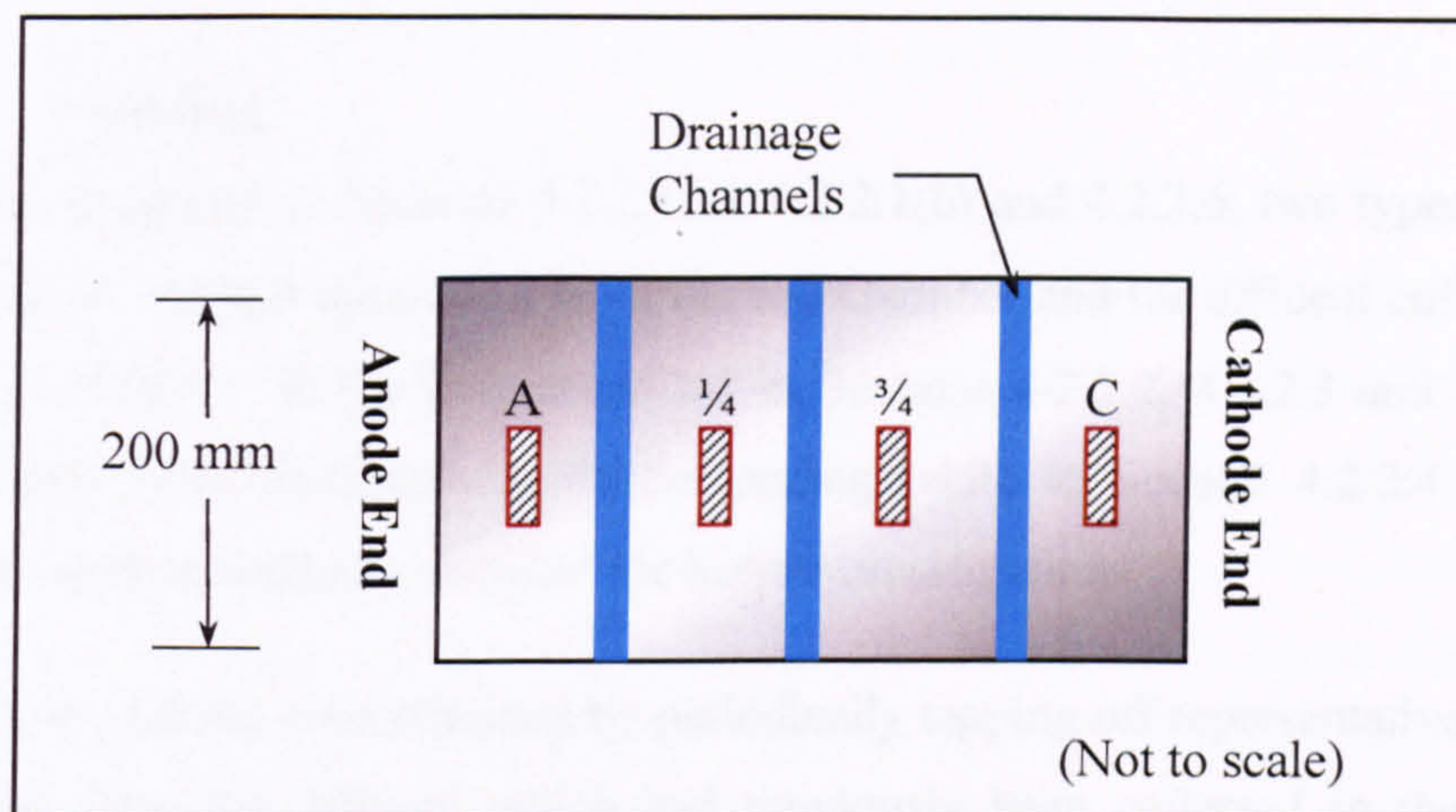


Fig 4.18 Plan Showing Sampling Locations

4.2.2.6 Control Experiments

The objective of the control experiments was to compare the metal extraction efficiency of soil flushing with that of the Two Process Approach method (where the electrokinetic process was combined with soil flushing during treatment). Therefore, the control tests essentially adopted the same methodology as was used in Section 4.2.2.1(b). In these tests, however, no electrical current was applied to the cell. Consequently, due to the hydraulic gradient existing between the cell ends, water was to continuously seep across the contaminated soil specimen without any external enhancement. It was expected that the seeping water, would also move along with the dissolved contaminant species, thereby effecting the cleaning process from one side of the cell to the other.

Since the hydraulic permeability of the soil material used in the study was very low (Section 4.1.1), no significant amount of water was expected to flow unaided across the specimen over the 5 weeks monitoring period. Therefore only one bench scale test, running up to 5 weeks, was carried out. At the end of the testing, soil samples were retrieved along the cell as in previous investigations. Samples were then taken for physical and chemical analysis. Additionally, the effluent was also monitored with time and periodically samples taken off for chemical analysis.

All the results are presented in Chapter 5 and discussed in Chapter 6.

4.2.3 Sampling

In the tests described in Sections 4.2.2.1(a), 4.2.2.1(b) and 4.2.2.6, two types of samples were retrieved; the soil specimens from the soil chamber and the effluent collected in the measuring cylinder. In the tests described in Sections 4.2.2.2, 4.2.2.3 and 4.2.2.5 only solid samples were retrieved for further testing while in Section 4.2.2.4 only liquid specimens were periodically sampled for further investigations.

The liquid specimens were obtained by periodically tapping off representative samples of about 30ml from the effluent which had previously been collected in the measuring chamber. The time interval between samplings ranged from one hour to a maximum of one week. Specimens taken off were for the determination of the target metal cations which had been electro migrated from the contaminated soil. All the results are presented in Chapter 5. Figure 4.19 shows sampling bottles used in the experimentation.

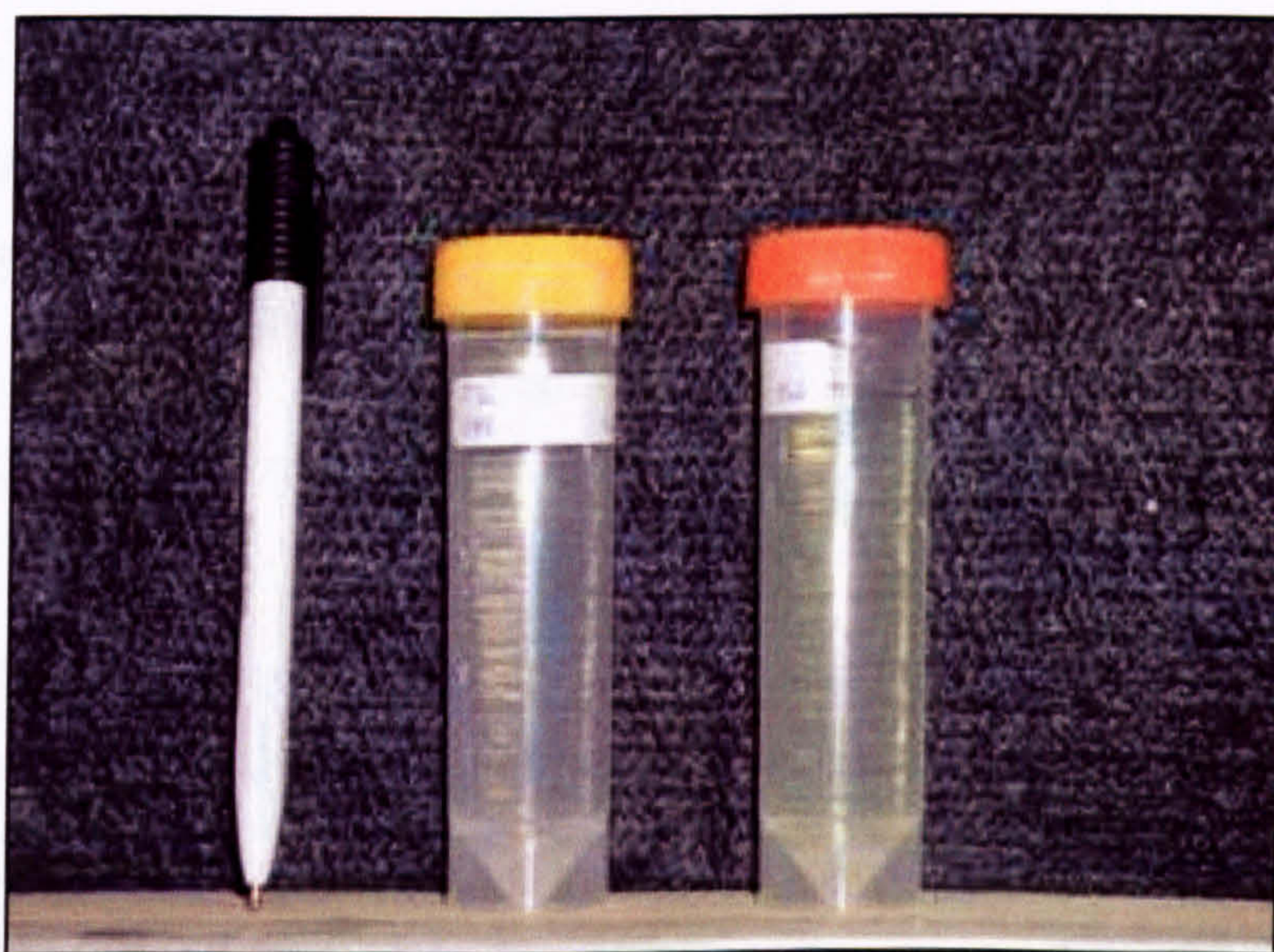


Fig 4.19 Sampling Bottles with Effluent

Soil samples were obtained on a weekly basis. Once the experiment had run to its target period (i.e. either 1, 2, 3, 4, 5 or 10 weeks), the power was switched off (except in the control experiments where there was no current applied). The tap on the plastic tube connecting the reservoir to the flushing chamber was closed off. The water at the cathode was pumped out. Sampling then began in the direction cathode to the anode with the

whole process being done as quickly as possible to prevent any redistribution of ions after the potential gradient had been removed.

The EKG electrode, at the cathode side, was first carefully pulled out making sure the process did not distort the soil in the chamber. Using a clean plastic spatula and spoon, a vertical face was formed at the cathode end by removing all soil material previously behind the electrode (cathode area). Plastic apparatus was selected as it was considered non reactive to the acidic or alkaline environment – and therefore could not chemically interfere with the samples being collected. Once the vertical plane had been formed at the cathode, two soil specimens of 5 grams each were sampled at the top and bottom of this position. Two samples were collected at each of these spots since one was for chemical analyses (Section 4.3.1) while the other was for physical tests (Section 4.4).

The procedure was repeated at $\frac{3}{4}$, $\frac{1}{2}$, $\frac{1}{4}$ and A positions. For each of these, though, two soil specimens of 5 grams each were collected at the top, middle and bottom of the vertical planes formed at these positions.

In order to minimise the effect of the boundary conditions, the samples at the top and bottom of the cell were collected approximately 1 cm away from the top and bottom surfaces respectively.

In total 28 samples were gathered from each test. Only four could be obtained at the cathode position as the material there had been eroded in the top third of the electrode areas.

Figure 4.20 below shows the cross sections of the sampling patterns at the mid cell (X-X) and cathode (Y-Y) positions, while Figure 4.21 shows pictures of a cut plane taken at different elevations.

4.3 Chemical Tests Procedures

Chemical tests were conducted mainly to determine the zinc (II) ions present. The methodology followed for the tests carried out on the soil and effluent specimens is presented in the subsections below.

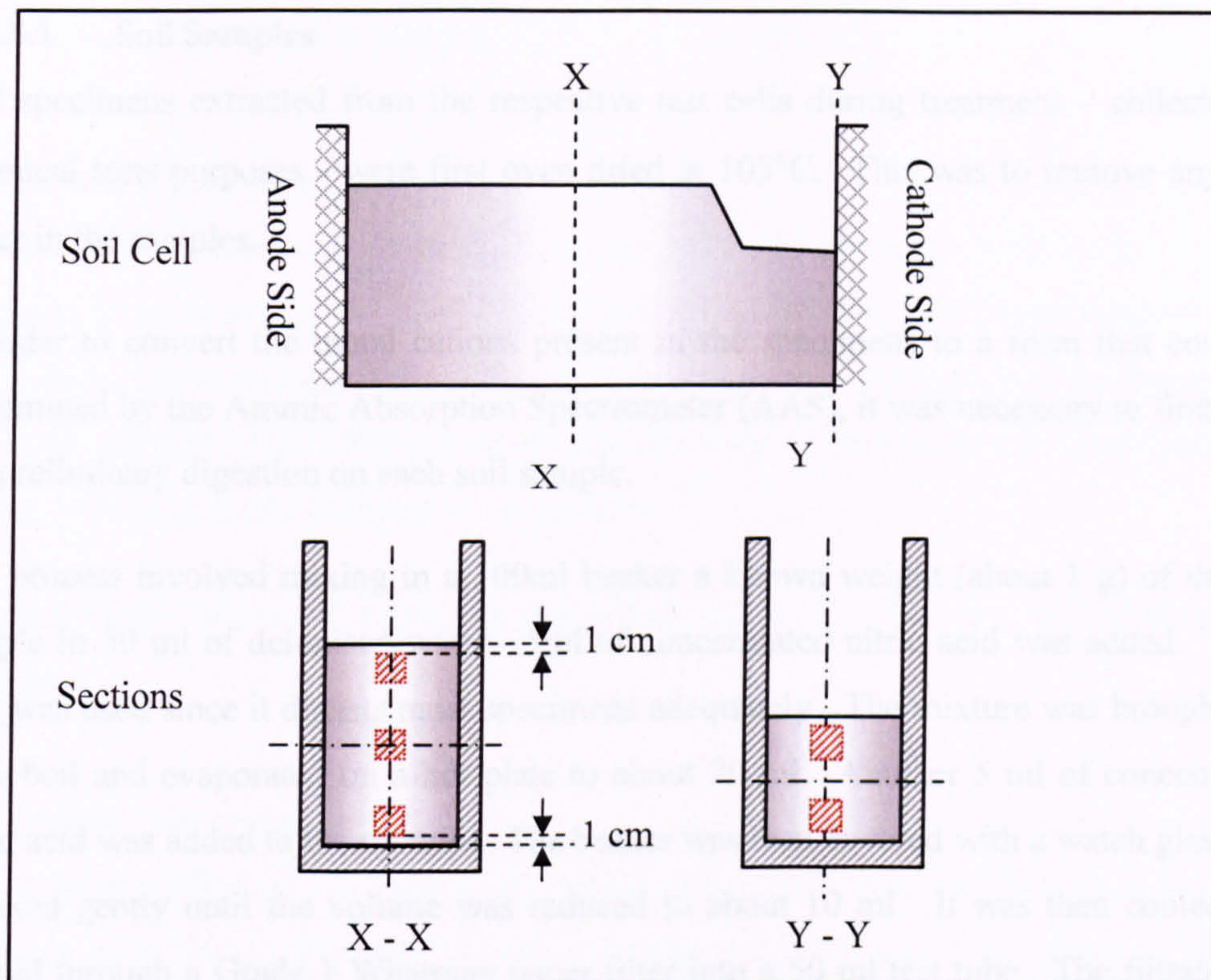


Fig 4.20 Sketch Showing Sampling Cross Sections at Two Different Positions

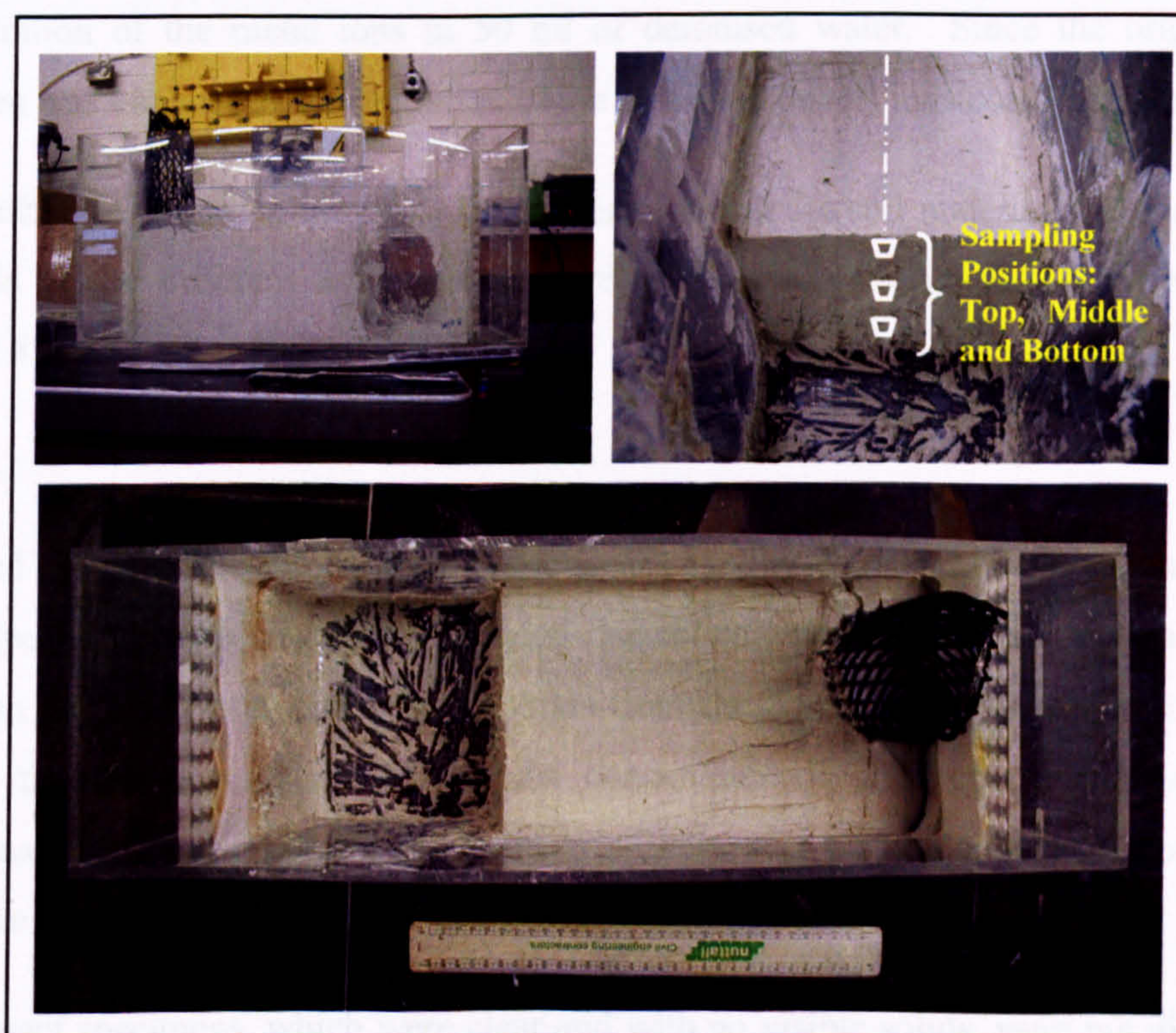


Fig 4.21 Pictures of Sampled Plane taken at Different Elevations

4.3.1 Soil Samples

Soil specimens extracted from the respective test cells during treatment – collected for chemical tests purposes - were first oven dried at 105°C. This was to remove any pore water in the samples.

In order to convert the metal cations present in the specimens to a form that could be determined by the Atomic Absorption Spectrometer (AAS), it was necessary to first carry out preliminary digestion on each soil sample.

The process involved mixing in a 100ml beaker a known weight (about 1 g) of the soil sample in 50 ml of deionised water. 5ml of concentrated nitric acid was added. Nitric acid was used since it digests most specimens adequately. The mixture was brought to a slow boil and evaporated on a hot plate to about 20 ml. Another 5 ml of concentrated nitric acid was added to the mixture. The beaker was then covered with a watch glass and refluxed gently until the volume was reduced to about 10 ml. It was then cooled and filtered through a Grade 1 Whatman paper filter into a 50 ml test tube. The filtrate was made up to the 50 ml mark with deionised water and mixed well. The filtrate was then put through a UNICAM 929 Atomic Absorption Spectrometer model which gave the concentration of the metal ions in 50 ml of deionised water. Since the original soil specimen was known the concentration of the adsorbed Zn (II) ions could be computed.

The results of the temporal metal ions concentration in the soil material, taken along the test cells of the different investigations, are presented in the graphs which appear in Chapter 5.

4.3.2 Effluent Samples

Collected effluent test samples were either clear or milky white solutions with suspended fines. Specimens with observed suspended fine solids were first filtered through Grade 1 Whatman paper filters to separate the solids from the liquids. The filtrate was then put through the AAS to determine the Zn concentration. The concentrations of the contaminant adsorbed on the solids retained on filters were then obtained by following the procedure already described in Section 4.3.1.

The effluent specimens, which were clear and with no visible solids, were put directly in the AAS and the respective Zn cation concentrations noted.

The results are also given in Chapter 5.

4.4 Physical Tests Procedures

Physical experiments were conducted only on solid soil samples. And the aim of these tests was to determine effect of the spatial and temporal changes in water content of the test cells on the metal extraction. As soon as samples were obtained from the bench scale test cells, the BS1377-2:1990 procedure was followed to determine the water content of each specimen from the different investigations.

The results are presented in the figures which appear in Chapter 5 and discussed in Chapter 6.

4.5 Quality Assurance

The reproducibility of the testing procedure and results was verified by conducting replicate experiments for one process (Section 4.2.2.1a) and two process (Section 4.2.2.1b) tests for a period of five weeks. The selected repetitions were based on the principle assumption that once the ultimate (end of five weeks) water content and contaminant distribution along the respective cells were comparable, then the interim weekly results were also expected to be repeatable.

Additionally, for each group of electrokinetic experiments, weekly current measurements within the group were compared. Since the main driving force during the electrokinetic process is current/voltage, it was assumed that if the respective interim weekly currents measured within each group were similar, then this would also be evidence of repeatability. On average 5 experiments were run for each test group with durations ranging from 1 to 5 weeks (Sections 4.2.2.1a, 4.2.2.1b, 4.2.2.2, 4.2.2.3, and 4.2.2.5).

Furthermore, to ensure that the test conditions were properly reproduced, the following precautions were taken:

- 1) New filter material, electrodes, and tubing were used for each experiment,
- 2) The reservoir tank (used in the two process experiments) and the testing tank were properly washed with tap water and then rinsed with deionised water to avoid cross

contamination between the experiments. No chemical detergents were used during washing,

- 3) The AAS was recalibrated after testing ten samples,
- 4) A mass balance analysis was performed for the One Process (Section 4.2.2.1a) and Two Process approach tests (Section 4.2.2.1b).

4.6 Summary of Tests Conducted

In Table 4.5, below, the overview of all the tests conducted in the study is shown.

Table 4.5 Summary of Tests Conducted

Experiment Number	External Experiment Tank Dimensions (mm)	Soil Cell Dimension (mm)	Flushing Water	Maximum Test Duration	No. of Runs	Main Investigation / Measured Parameters	Number of Samples Retrieved and Tested / Readings	Comments
S3_05	500 x 200 x 250	410 x 200 x 150	Yes	5 Weeks	5 + 1*	1. Zn Concentration	90	Water flushing at the Anode throughout the experiment and an applied continuous direct current.
						2. WC ¹ with time	80	
						3. Current with time	72	
						4. Effluent Volume	15	
S5_01	500 x 200 x 250	410 x 200 x 150	No	5 Weeks	5 + 1*	1. Zn Concentration	90	No irrigation at the Anode but having an applied continuous direct current
						2. WC with time	80	
						3. Current with time	66	
						4. Effluent Volume	15	
S3_07	500 x 200 x 250	410 x 200 x 150	Yes	10 Weeks	4	1. Zn Concentration	60	Water flushing at the Anode and current applied intermittently (periodically 24 hours on and 24 hours off)
						2. WC with time	60	
						3. Current with time	40	

Table 4.5 Summary of Tests Conducted (Continued)

S3_06	500 x 200 x 350	410 x 200 x 300	Yes	5 Weeks	5	1. Zn Concentration	75	Same as S3_05, but with test sample height doubled to 300mm
						2. WC with time	75	
						3. Current with time	40	
pH_C01	500 x 200 x 250	-	Yes	5 Weeks	1	pH in localised chambers with time	35	pH of water in the partitions
pH_03	500 x 200 x 250	-	Yes	5 Weeks	5	1. Zn Concentration	60	Clean water in Chambers every after 24 hours
						2. WC with time	60	
Control	500 x 200 x 250	410 x 200 x 150	Yes	5 Weeks	2	1. Zn Concentration	18	Treatment with water flushing only at one end of the test cell
						2. WC with time	32	
						3. Effluent Volume	19	

¹ WC – Water Content

* Additional test conducted as a repeat of the 5 week test

RESULTS

5.0 Introduction

This chapter presents in detail the results of the bench-scale One Process and Two Process Approach experiments performed to study the electrokinetic remediation of heavy metals from fine grained soils using EKGs as electrodes. The respective responses are primarily presented with respect to: (a) the temporal variations of the electrical current measured in the test cells, (b) the temporal and spatial water content changes in the soil specimens, and (c) the temporal and spatial zinc ion (Zn^{2+}) concentrations in the soil samples. The outcomes are compared to identify the effects of: water flushing, soil depth, intermittent electrical currents, and replenishing draining chambers along the soil profile with deionised water, on the migration characteristics of the Zn^{2+} during treatment.

The results of the pH of the electrolyte along the cell length are given. These are followed by those of volumes of the effluents separately collected during treatment of the test soil specimens, under the Control, the One Process and the Two Process Approach conditions. The respective solution pH and concentrations of Zn^{2+} in the effluent water and suspended solids are given. The quality of the data is then assessed. Finally, a summary of the findings and the conclusions of the chapter are provided.

In this chapter, however, little attempt is made to explain the patterns or the observed behaviours implications to contaminant extraction. Detailed discussions and analyses especially with respect to the migration of the metal cations are presented in Chapter 6.

5.1 One Process Approach

This approach was operated under ‘closed anode’ conditions so that no water was available to flush through the test soil specimen. The closed experiments were performed to gain a basic understanding of migration of the heavy metal cations under electrokinetic influence without any external enhancement agent as well as to compare the metal removal efficiency with soil specimens enhanced with an external agent. Each

experimental specimen had a length of 400mm, width of 200 and was 150mm in depth. A constant voltage of 18VDC, creating a constant voltage gradient of 0.5 V/cm, was applied across the soil specimen for all the tests. The full details of the testing procedures are already set out in Sections 4.2.2.1, 4.3 and 4.4. This section, therefore, presents the laboratory results obtained under this approach in terms of the temporal variations in electrical current supplied to the test cell, and the spatial changes of WC and Zn^{2+} within the specimen soil mass.

(a) *Electrical Current*

The electrical currents from all five tests, read periodically from the power supply, over a five week programme are plotted against time in Figure 5.1. It is observed that the data from all five cells aligned with a best fit curve thereby demonstrating the repeatability of the tests. A line of best fit through the all data points, which provides an 'average', shows an identical pattern i.e. with the highest current being measured at the beginning of each experiment. The average initial current was 48 mA reducing to practically zero by the end of the fifth week of testing.

Weekly average electrical current values from the five tests were computed and tabulated in Table A5.1 in the appendix. The weekly percentage changes from Table A5.1 were then plotted in Figure 5.2.

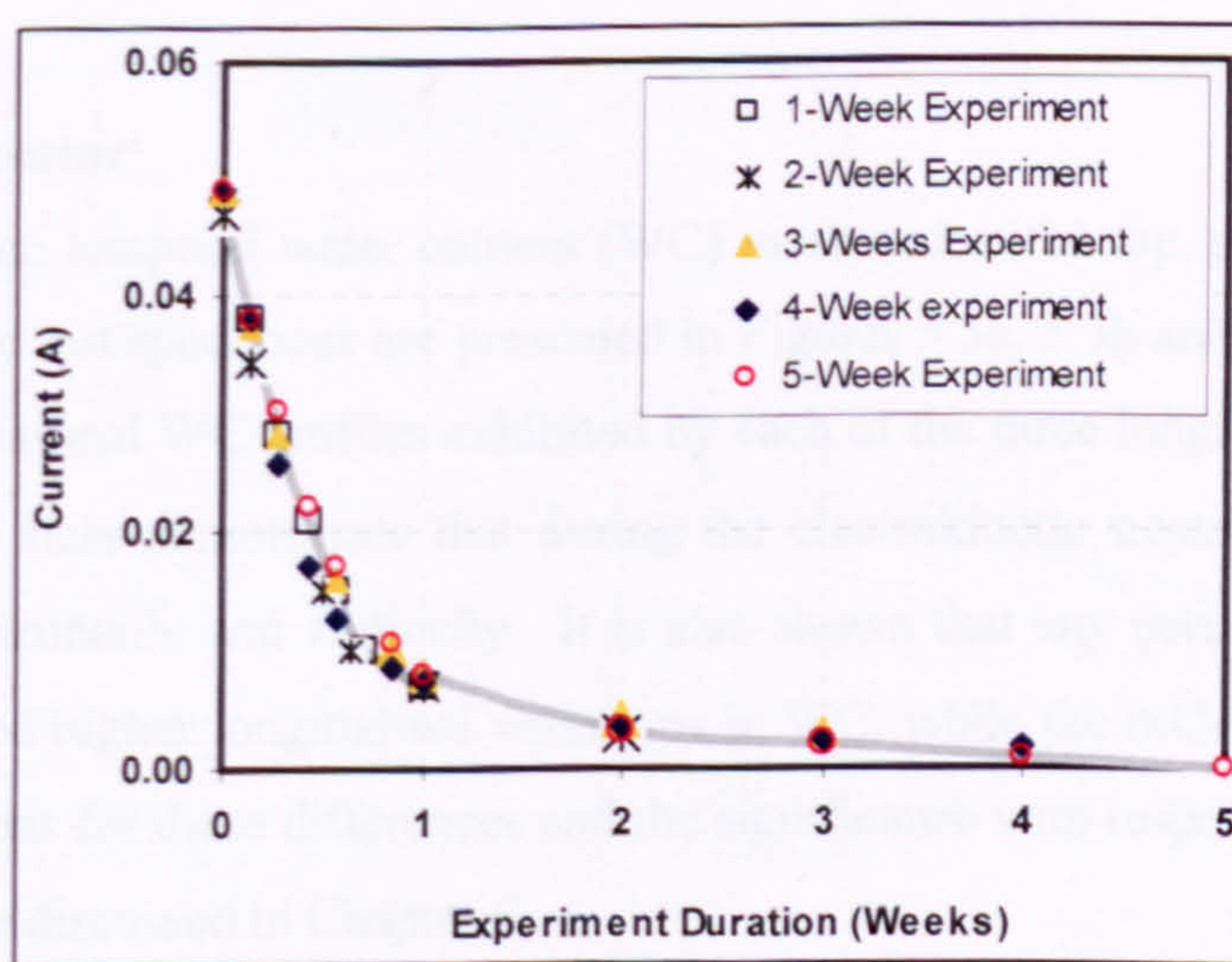


Fig 5.1 Variation of Current with Time with No Flushing at Anode

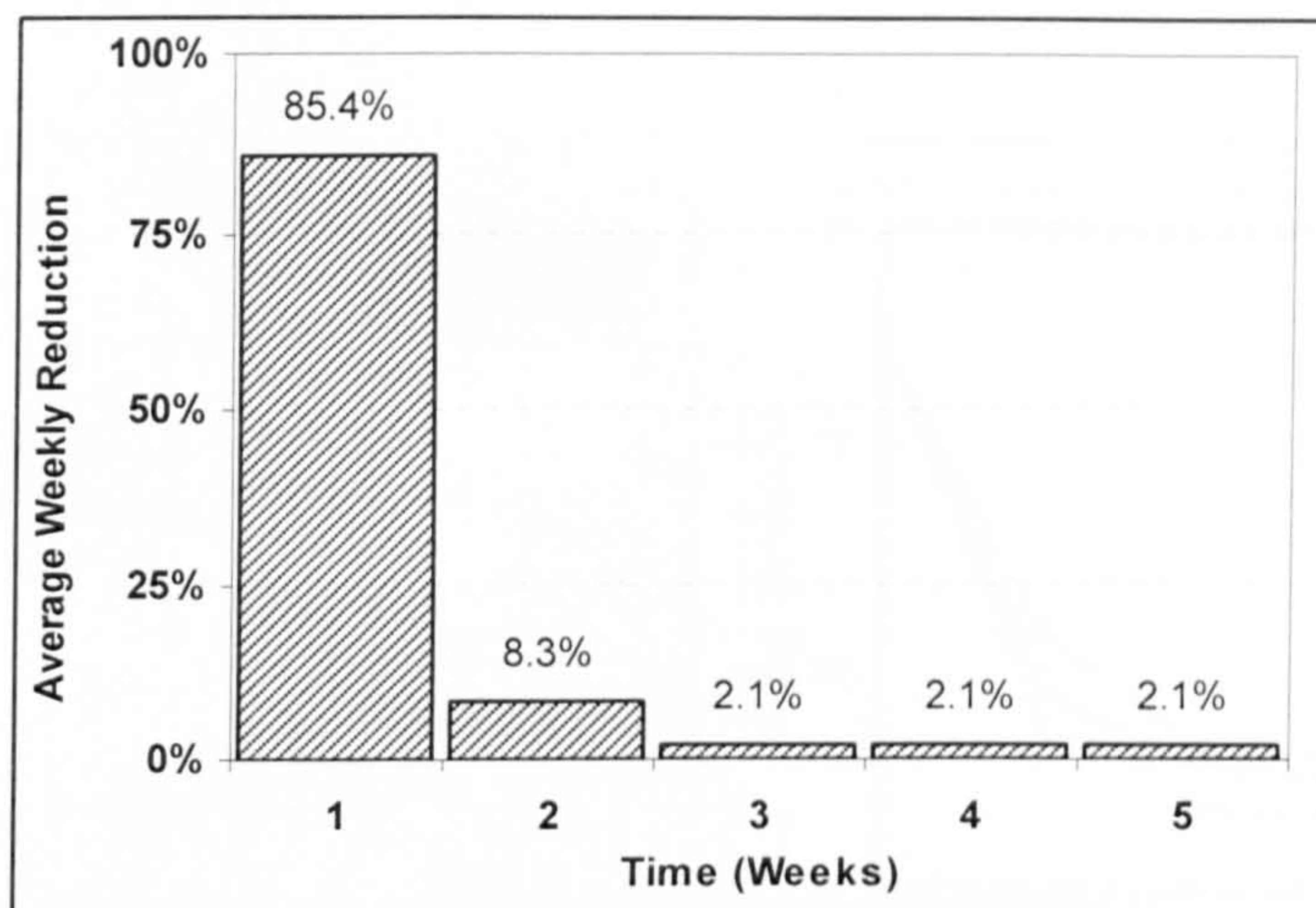


Fig 5.2 Weekly Differences in Current with no Flushing at Anode

Comparison of the weekly changes shows that by the end of the first week, the current had reduced by nearly 85% of the original value, and by almost 8% in the following week. Therefore, by the end of the first two weeks alone, the current had significantly and non linearly dropped by 93.7%, demonstrating that the largest amount of electrical energy was consumed during the initial stages of the treatment. Beyond the second week, however, the decrease per week stabilised to 2.1% (equivalent to about 0.001A).

The amount of voltage measured in the sample during each test, and hence the electrical efficiency of the system is discussed in Chapter 6.

(b) Water Content

The results of the temporal water content (WC) measured at the top, middle and bottom thirds of the five test specimens are presented in Figures 5.3a, 5.3b and 5.3c respectively. The weekly positional WC profiles exhibited by each of the three longitudinal sections of the treated soil mass demonstrate that during the electrokinetic treatment, the soil WC varied both horizontally and vertically. It is also shown that any particular time the top third experienced higher longitudinal variations in WC, while the middle section had the least. The reasons for these differences and the significance with respect to interpretation of the results are discussed in Chapter 6.

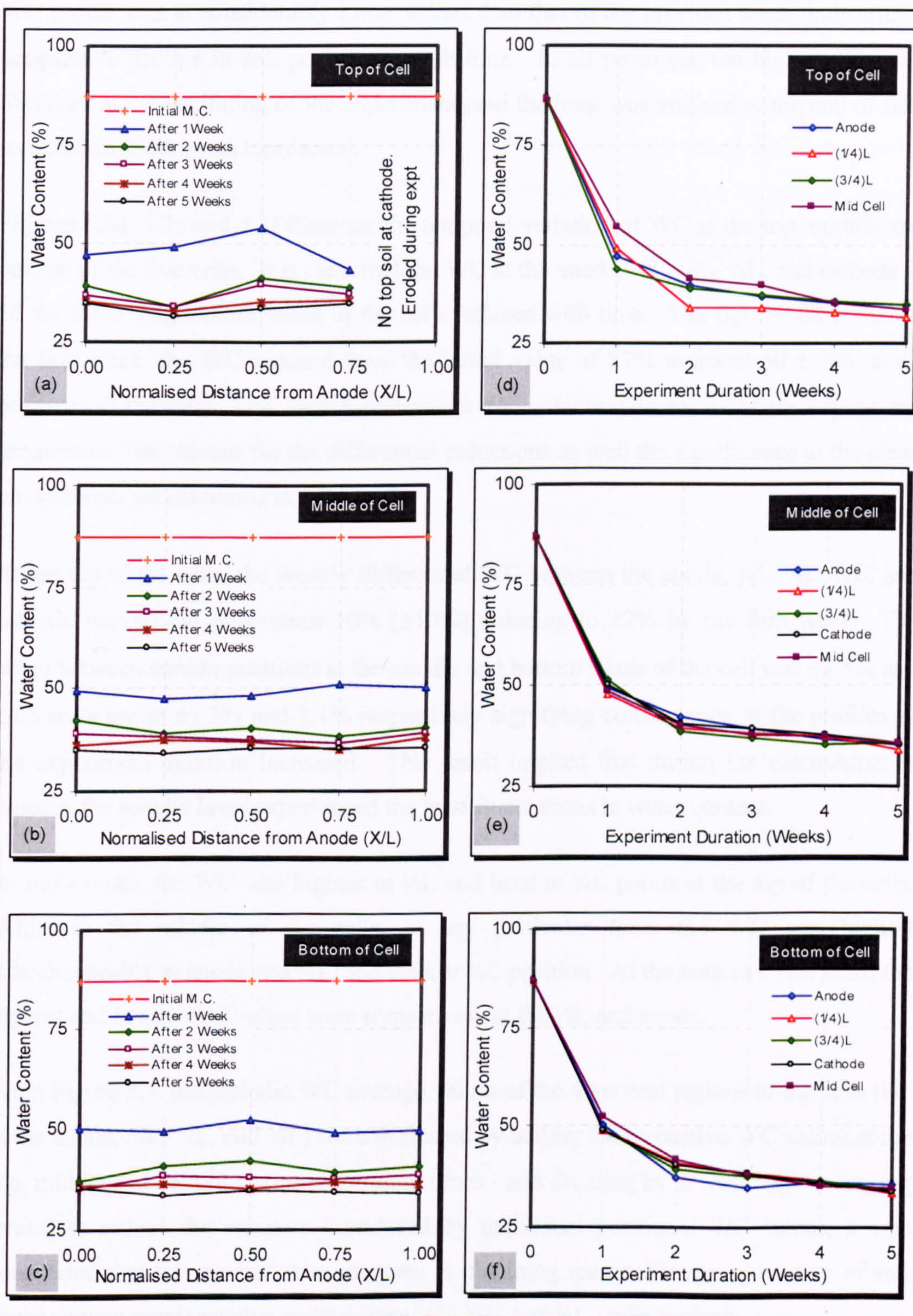


Fig 5.3 Variation of WC: (a, b, c) along cell and (d, e, f) with Time - for no Flushing at the Anode

In all the three longitudinal sections presented in Figures 5.3a, 5.3b and 5.3c, each weekly WC profile was at considerably lower values than that of the previous week, indicating a progressive decline in soil pore water with time. In all positions, the highest WC was observed at the beginning of the experiment, and the least was attained at the end of fifth week when testing was terminated.

Figures 5.3d, 5.3e and 5.3f illustrate the temporal variation of WC at the top, middle and bottom of the five cells. It is clear that the WC at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$, and cathode at all the three longitudinal thirds of the cells reduced with time. The figures show that in the first week, the WC reduced from the initial value of 87% to about $50 \pm 5\%$, at all positions of the cells. The weekly percentage WC reduction decreased as the experiment progressed. The reasons for the differential reductions as well the significance to the clean up operation are discussed in Chapter 6.

At the top of the cells, the weekly differential WC between the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$, and cathode was within plus/minus 10% ($\pm 10\%$) reducing to $\pm 2\%$ by the fifth week. The range between similar positions at the middle and bottom thirds of the cell was $\pm 3.5\%$ and $\pm 4.5\%$ reducing to $\pm 1.3\%$ and 2.1% respectively signifying convergence of the profiles as the experiment duration increased. This result implied that during the electrokinetics process, the middle layer experienced the least fluctuations in water content.

At most times, the WC was highest at $\frac{1}{2}L$ and least at $\frac{1}{4}L$ points at the top of the cells. While in the middle of the cells, at any particular time, the WC was highest interchangeably at anode and $\frac{1}{2}L$, and least at $\frac{3}{4}L$ position. At the bottom of the cells, the highest and lowest WC values were respectively at the $\frac{1}{2}L$ and anode.

From Figure 5.3, the periodic WC average values of the 4 vertical regions of the cells (i.e. at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, and $\frac{3}{4}L$) were evaluated by adding the respective WC values at the top, middle and bottom - at corresponding times - and dividing by 3. Although averaging tended to reduce the variance introduced by individual positional WC values, it was considered that this method was adequate in obtaining reasonable approximation of soil water content representative at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, and $\frac{3}{4}L$ vertical planes.

At the cathode, however, the average WCs were computed by adding the WC values at the middle and bottom of the cathode end, at the respective test durations, and dividing by 2. This was because the top soil at the cathode was dispersed into solution and filtered into the effluent chamber as soon as the experiment was started. In fact, by the end of the first week of investigation, the top third of the soil around the cathode had been eroded and washed into the effluent chamber. This observation is presented in greater detail in Section 5.5.

The obtained average values were then plotted in Figures 5.4 and 5.5 which respectively depict the typical weekly average WC profiles at normalised distances from the anode and the relationship between the elapsed time and the average WC for specific sampled points along the testing cell. The plots demonstrate that:

- 1) Generally, the WC at any specified section within the soil specimen mass decreased with time, with the rapid drop occurring during the first week of operation. The weekly decrease in soil water reduced with increase in test duration.
- 2) For the first and second weekly durations, the soil pore water was marginally highest at the mid cell position and lowest at the either ends of the cell.

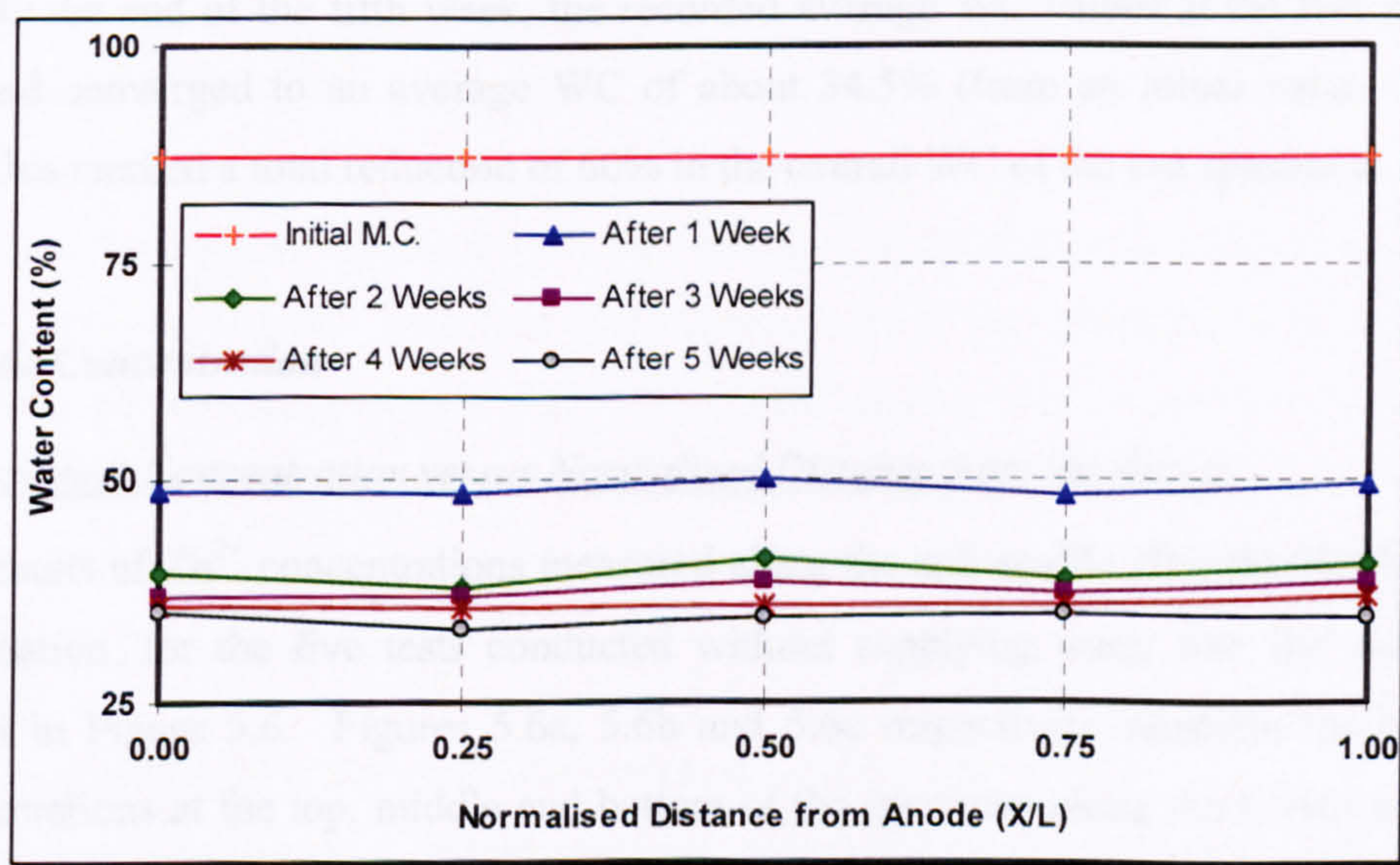


Fig 5.4 Variation of Average WC along Cell for no Flushing at the Anode

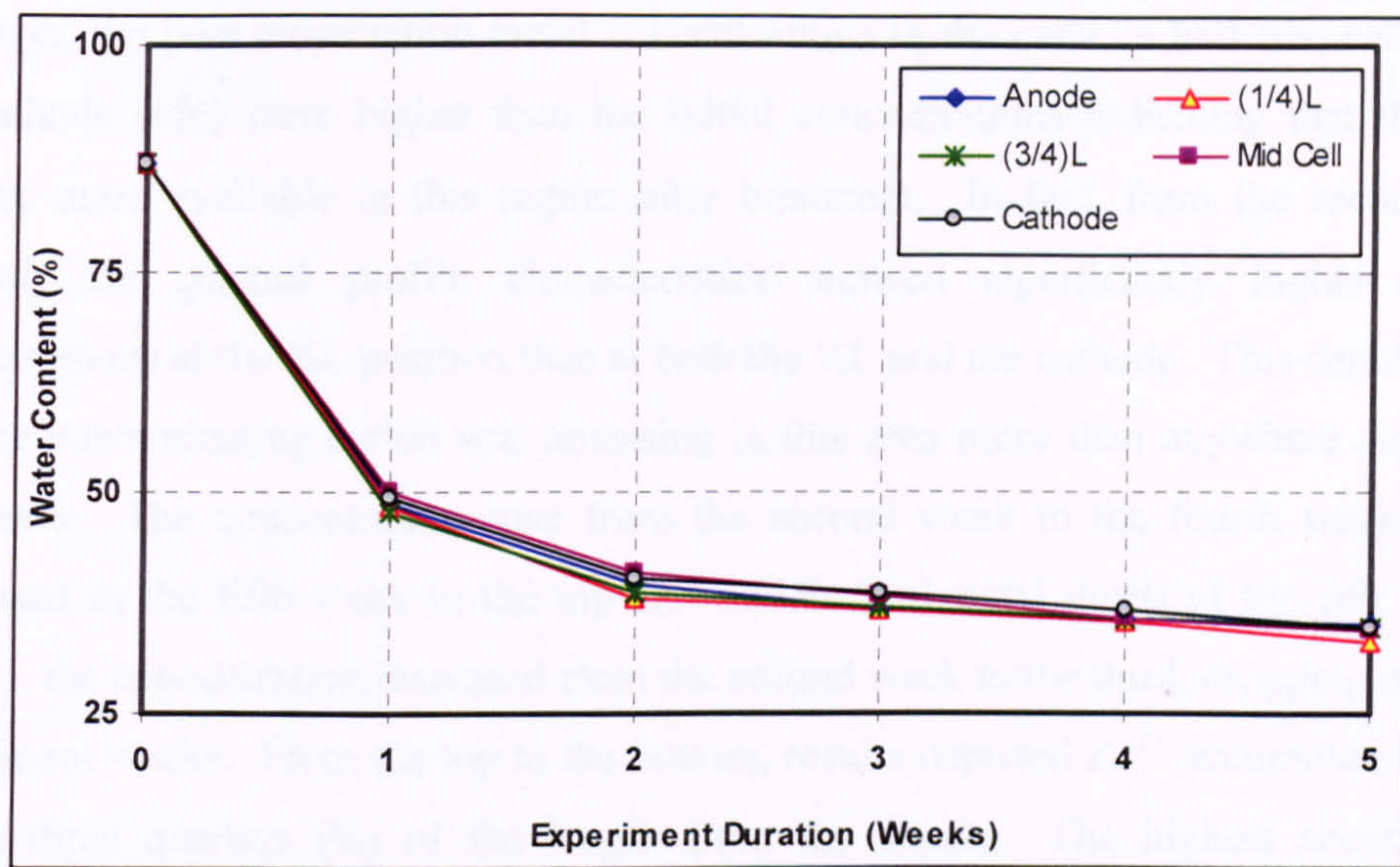


Fig 5.5 Variation of Average WC with Time for no Flushing at the Anode

- 3) From the third week onwards the average WC was nearly the same along the entire length of the test specimen. Therefore, as the experiment progressed, the average spatial WC in the specimen converged to about the same values. By this period, the WC had reduced to nearly 44%.
- 4) By the end of the fifth week, the recorded average WC values at the five positions had converged to an average WC of about 34.5% (from an initial value of 87%). This marked a total reduction of 60% in the overall WC of the test specimen.

(c) Zinc Concentrations

Contaminant Concentration versus Normalised Distance from the Anode

The results of Zn^{2+} concentrations measured along the soil profile after the electrokinetic remediation, for the five tests conducted without supplying water into the anode, are shown in Figure 5.6. Figures 5.6a, 5.6b and 5.6c respectively illustrate the available concentrations at the top, middle and bottom of the specimen along the horizontal thirds of the cells. It is clear that the available Zn^{2+} concentrations at the anode half (the half of the cell on the anode side) did not exceed the original metal concentration value of 52mg/kg during treatments - it progressively decreased due to electrokinetic treatment.

However, the post remediation metal concentrations in the cathode half (the cell half on the cathode side) were higher than the initial concentrations indicating that the metal became more available in this region after treatment. In fact, from the second week onward, the general profile characteristics showed significantly higher metallic concentrations at the $\frac{3}{4}L$ position than at both the $\frac{1}{2}L$ and the cathode. This demonstrated that the contaminating cation was amassing in this area more than anywhere else in the soil mass. The concentration rose from the second week to the fourth week until it decreased in the fifth week in the top and middle horizontal thirds of the cell. At the bottom, the concentration increased from the second week to the third, dropping off in the subsequent weeks. From the top to the bottom, results depicted Zn^{2+} accumulation in the region three quarters ($\frac{3}{4}$) of the length from the anode. The highest accumulation occurred in the middle longitudinal third of the cells where the pyramid like tip peaked at the 300mg/kg mark. This decrease in metal ions in one half subsequently followed by the increase in another, confirmed the migration of these positive ions in the direction of anode-to-cathode.

Contaminant Concentration versus Time

Figures 5.6d, 5.6e and 5.6f respectively show the variation with time, of the Zn^{2+} concentrations at along the top, middle and bottom horizontal thirds of the test cells.

Top of the Cells (Figure 5.6(d))

The contaminant concentration decreased with increase in test duration at the anode and $\frac{1}{4}L$. In both cases the highest drop in Zn^{2+} occurred in the first week of clean up. For the $\frac{1}{4}L$, however, the gentle reduction slope between week one and three is followed by a steeper one from weeks three to five. At $\frac{1}{2}L$, the amount first increased during the first week by 18% before decreasing to 12.5mg/kg which was 4 times less than the initial concentration. The concentration then kept decreasing till the fourth week but picked up just slightly to 11.3mg/kg in the fifth week.

At $\frac{3}{4}L$ the concentration of metal ions originally reduced by a mere 2.4mg/kg (4%) in the first week of testing before increasing in the second week. According to the graph, there was rapid accumulation in the metal concentration between the second and fourth weeks with the peak being 196mg/kg. This was almost four times the original concentration of

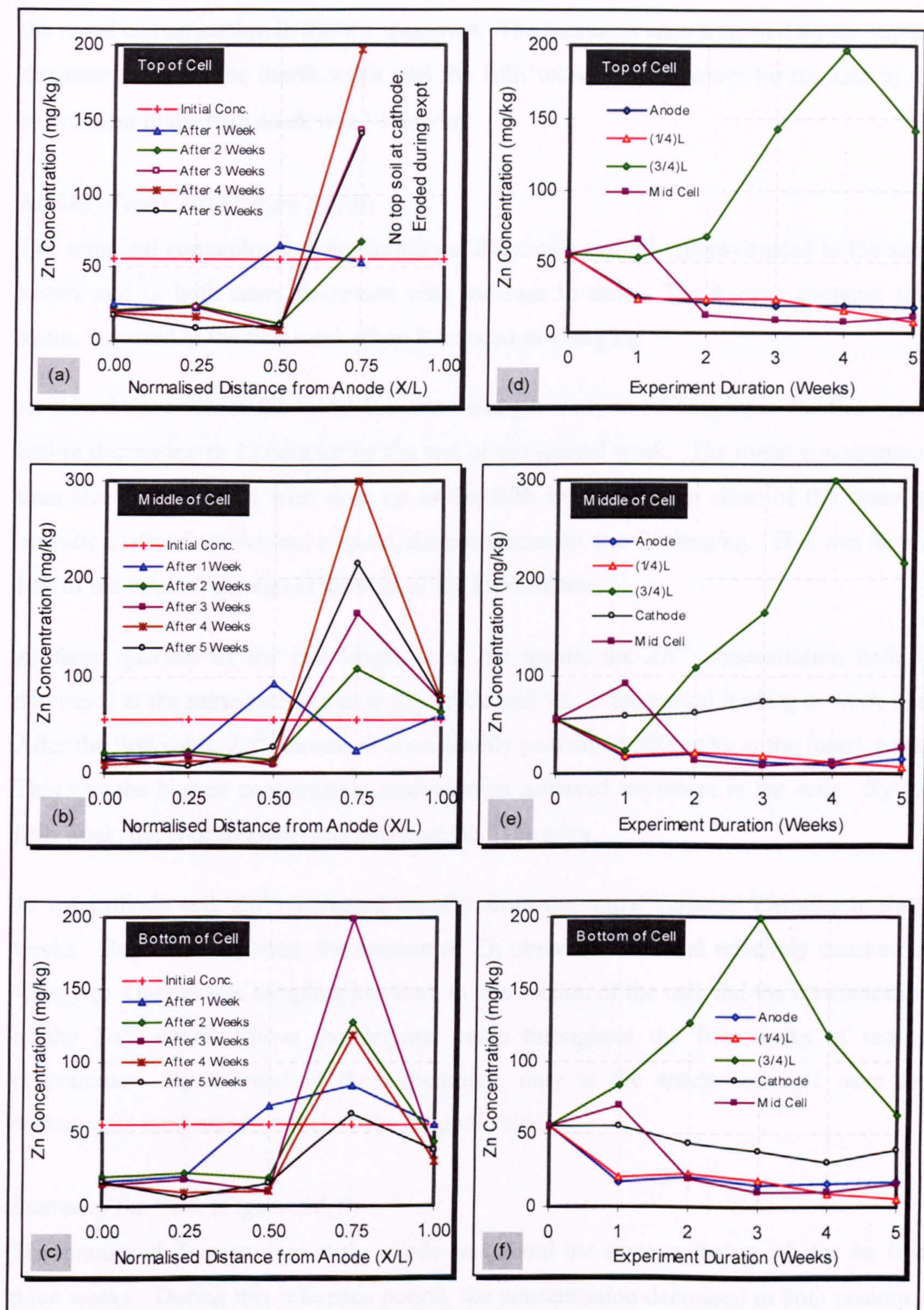


Fig 5.6 Variation of Zinc Concentration (a, b, c) along cell and (d, e, f) with Time - for no Flushing at the Anode

the metal contamination in the test specimen. The increases were followed by subsequent decrease between the fourth week and the fifth week. The amount by the end of the experiment in the fifth week was 141mg/kg.

Middle of the Cells (Figure 5.6(e))

The temporal contaminant concentration at the anode and $\frac{1}{4}L$ approximated to the same values and in both cases decreased with increase in time. The highest decrease rate, again, occurred in the first week when it reduced to 17mg/kg.

At $\frac{1}{2}L$, the amount of the metal increased straight away to 92.5mg/kg in the first week, before decreasing to 12.6mg/kg by the end of the second week. The metal concentration then steadily increased with time up to the fifth week. By the close of the clean up operation, after 5 weeks had elapsed, the concentration was 26.9mg/kg. This was almost half of the original amount at the start of the experiments.

At three quarters of the cell length from the anode, the Zn^{2+} concentration initially decreased at the same rate as that at the anode and $\frac{1}{4}L$ in the period leading to week one. After the first week, Zn^{2+} increased considerably peaking at 300mg/kg at the fourth week. This was the highest contaminant concentration achieved anywhere in the cells. By the fifth week, the concentration had decreased to 215mg/kg.

At the cathode end, Zn^{2+} increased steadily from the initial value to 75mg/kg in three weeks. Beyond this period, the amount of Zn observed remained relatively constant at 75mg/kg. Only at this sampling position, in this section of the cell, did the concentration of the Zn^{2+} remain above the original value throughout the five weeks of testing programme. By the end of the experiment, only at the anode cell half were the contaminant concentrations below the original value.

Bottom of the Cells (Figure 5.6(f))

The amount of Zn measured at the anode was about the same as that at $\frac{1}{4}L$ for the first three weeks. During this reference period, the concentration decreased in both positions with increase with time. However, while in the following two weeks of electrokinetic process, the concentration remained constant at the anode end, it did continue to decrease at $\frac{1}{4}L$.

At $\frac{1}{2}L$ the behaviour was the same to that of the similar position in the middle third layer of the cells. There was first an increase within one week, which was followed by a gradual decrease in metal ions adsorbed.

At $\frac{3}{4}L$, the concentration of Zn^{2+} increased as soon as the experiment started running. This lasted until three weeks had elapsed. After which there was a drop in concentration values.

At the cathode region, the contaminant concentration reduced marginally by 0.3mg/kg (0.5%) in one week. Beyond this period, the concentration dropped further till the fourth week when it reached 30mg/kg before picking up in the last week to 38mg/kg.

Overall

Results for the three horizontal longitudinal specimen layers showed that:

- 1) For nearly four weeks of testing, and in all the three layers, the temporal contaminant concentration at the anode was about the same that at $\frac{1}{4}L$ and in both cases decreased with increase in time.
- 2) Where as in the first week, the lowest contaminating cation concentrations were obtained at the anode and $\frac{1}{4}L$, between the second and the fourth week, the least measured values were at $\frac{1}{2}L$. By the fifth week, the lowest Zn^{2+} concentration was at $\frac{1}{4}L$.
- 3) The highest accumulated Zn was found at $\frac{3}{4}L$ between the third and the fourth week. The individual layer positional peaks were reached after three weeks at the bottom and four weeks at the top and middle sections. This implied that the cation concentration first peaked at the bottom layer a week earlier, before peaks were observed at the top and middle layers. The peaks were recorded at 196, 300 and 200 mg/kg at the top, middle and bottom longitudinal sections respectively. These values indicate that the highest accumulation of metal ions was obtained in the middle layer sandwiched between the boundary layers of the top and bottom.

Average Values

From Figure 5.6 above, the average weekly Zn^{2+} concentration at respective cells positions, were computed and plotted in Figures 5.7 and 5.8. The same method used to obtain the weekly WC averages along the test specimens lengths, in Section 5.1(b) above, was used to determine the averages of the respective positional Zn^{2+} concentrations. Figure 5.7 illustrates the average spatial variations of the contaminating metal ions along the cell length. While, Figure 5.8 presents the graph of the average migration behaviour of the metal ions, at specific positions in the cell, versus the experiment duration.

From Figure 5.7, it is re-affirmed that the movement of the Zn^{2+} was in the direction towards the cathode. After the initial week, the average concentrations of the metal at the anode, $\frac{1}{4}L$ and mid cell were lower than the start up value of 55.5mg/kg. The average metal concentration in this anode half of the cell was about the same as depicted by the near horizontal second, third, fourth, and fifth weekly concentration profile plots. By the fifth week, the Zn^{2+} in this specimen half had reduced by about 43.5mg/kg (approximately 78%). However, the results show considerable increases at $\frac{3}{4}L$. In this position, except in the first week, all other average weekly Zn^{2+} concentrations were higher than the original. The maximum peak was that of the four week profile, which at 205mg/kg, made it approximately 4 four times the original amount at the start of the experiment. By the end of the investigations, the concentration at the $\frac{3}{4}L$ had dropped to 140mg/kg, still making this region the most contaminated in the whole specimen.

The weekly profiles also depict that the metal concentration at the cathode position, throughout the testing, remained nearly the same, as that at the start of the investigation. The reason for this occurrence is discussed in Chapter 6.

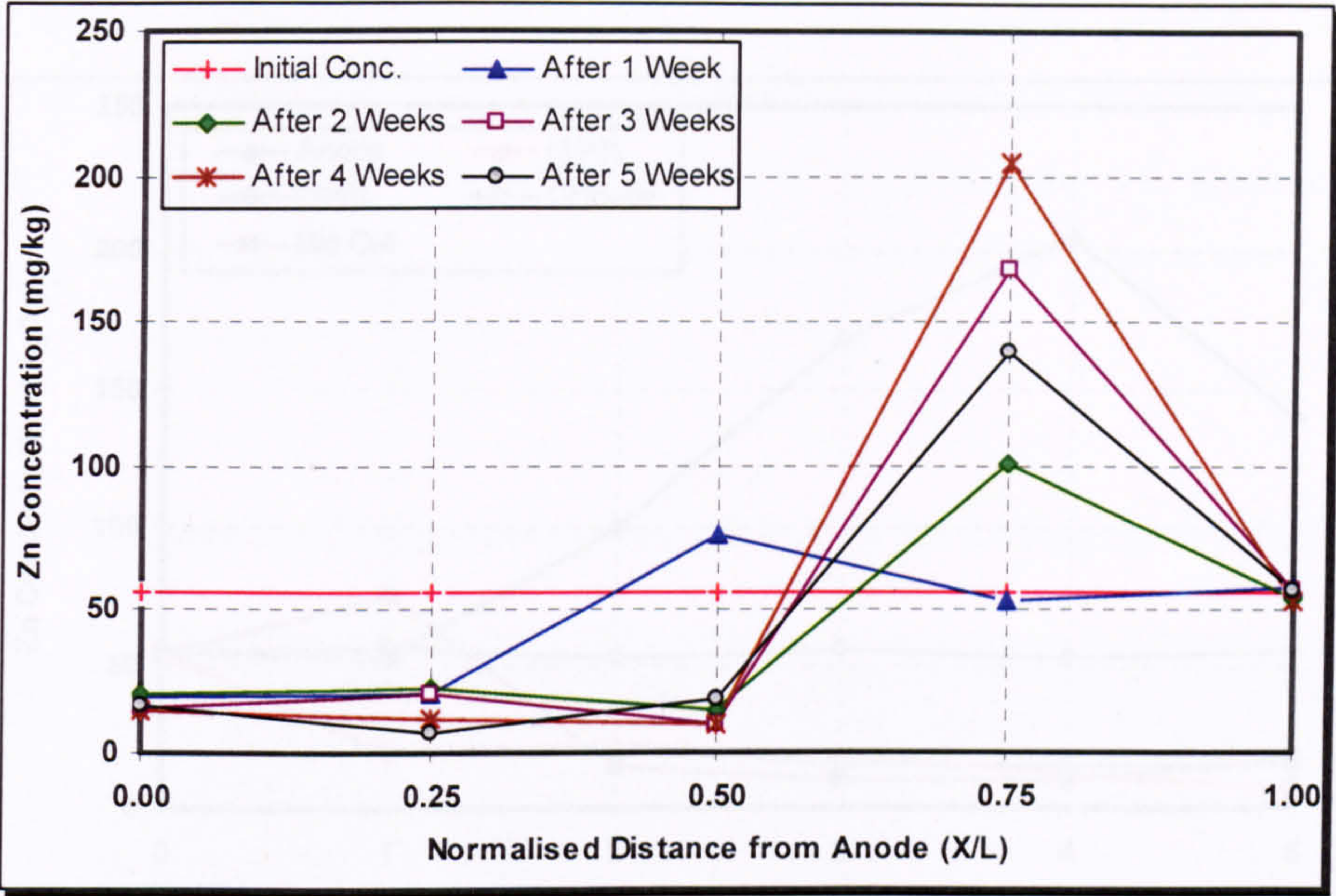


Fig 5.7 Variation of Average Zinc Concentration along Cell - no Flushing at the Anode

In Figure 5.8, the variation of the recorded average Zn^{2+} with time is presented. The concentration of the metal ions straight away decreased in the first week at the anode and $\frac{1}{4}L$ to 20mg/kg (reduction of 64%). At the anode, though, the average concentration remained about the same until the fifth week, while at $\frac{1}{4}L$ it kept dropping at rate of 3.4mg/kg per week. By the fifth week, the concentration at $\frac{1}{4}L$ had decreased to 6.6mg/kg.

Further more, the graph shows that the observed decrease in concentrations at the anode and $\frac{1}{4}L$ during the first week resulted in an increase to 75.6mg/kg at the mid cell area. This was followed by a decrease to 14.5mg/kg in the second week. The decrease continued gradually for the next two weeks before a gentle increase was experienced in the last week of testing.

At the positions between $\frac{3}{4}L$ and the cathode, little cation activity was evident initially as the average metal concentrations were nearly the same as at the start. However, at $\frac{3}{4}L$, the following three weeks of electrokinetic operation were followed by sharp accumulation in the metal concentration. The average increase in this period was 50.6mg/kg per week, peaking at the fourth week to 205mg/kg. The concentration

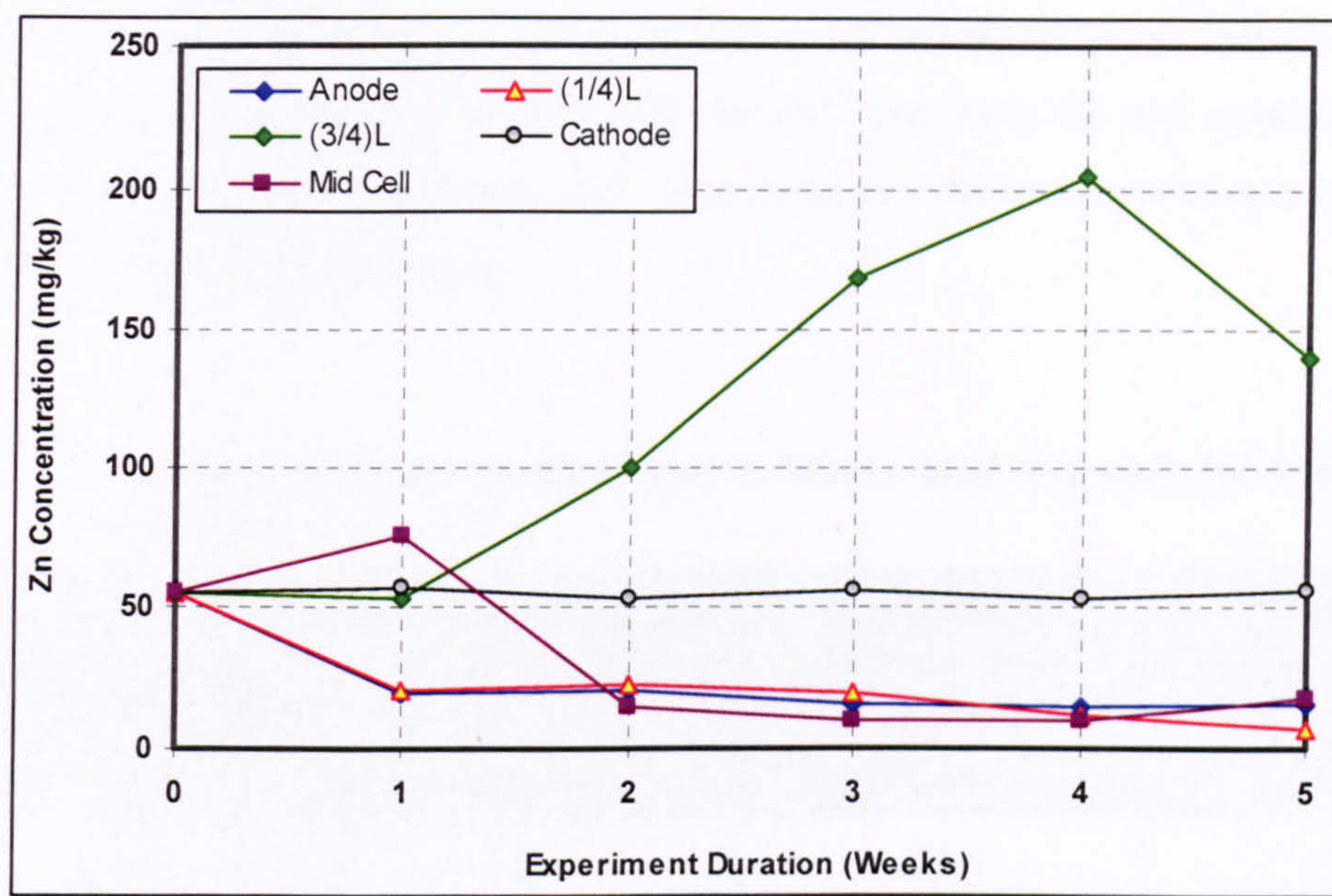


Fig 5.8 Variation of Average Zinc Concentration with Time - no Flushing at the Anode

ultimately decreased to 140mg/kg in the last week of testing. This made the position $\frac{3}{4}L$ to be the most contaminated by the end of the experiment with the contaminant levels being 2.5 times the original value. On the other hand, throughout the experimentation, the average concentration at the cathode fluctuated within ± 2.0 mg/kg as the current run through the sample. On a whole it remained about the same over the entire reference period. Zinc ions, although attracted toward the cathode, were precipitated in the high pH regions of $\frac{3}{4}L$ (Section 5.4) causing an accumulation of the metal ions there. It is also probable that the high pH at the cathode caused adsorption of the Zn^{2+} onto the soil causing the contaminant to be immobile there also. Any further Zn^{2+} migrating from $\frac{3}{4}L$ with the electroosmotic water probably continued and filtered into the effluent chamber. This could have been the cause of a general constant Zn concentration at the cathode.

Comparatively, the average values reveal that as the metal concentrations reduced initially at the anode and $\frac{1}{4}L$ positions, the concentration levels rose at the $\frac{1}{2}L$ area. In the following week, the considerable decrease in metal cations at $\frac{1}{2}L$ was matched by an accumulation of the same at $\frac{3}{4}L$. From the end of the second week, as the amount of the contaminating cations was evidently still reducing in the anode half of the cell, the amount at the $\frac{3}{4}L$ continued to rise.

The average residual metal ions, still present in the soil mass, by the end of the fifth week (i.e. end of experiment) were read off from Figure 5.8 and presented in Table 5.1 below. The respective values were compared with the Zn^{2+} present in the soil specimen at the start of the investigation to determine the net increase or reduction in metal concentrations at each of the five sampled regions.

Table 5.1 Average Zn Concentration after 5 Weeks Had Elapsed: No Flushing at Anode

Position along Cell	Zinc Concentration after 5 Weeks (mg/kg)	Concentration Increase (+) / Decrease (-) (mg/kg)	Percentage Changes (+/-) (%)
Anode	16	-39.5	-71
$\frac{1}{4}\text{L}$	6.6	-48.9	-88
Mid Cell	18	-37.5	-68
$\frac{3}{4}\text{L}$	140	84.5	152
Cathode	56.3	0.5	1.4

The comparison results in Table 5.1 show that:

- 1) The best treatment outcome (in terms of contaminant species extraction) was achieved at $\frac{1}{4}\text{L}$, where 88% of the original metal ions present were removed. This was followed by the removal at the anode and mid cell regions with the average respective reductions in the metal concentrations of 71% and 68%.
- 2) The worst treatment results were at the distance a quarter from the cathode where the Zn^{2+} increased by 152%.
- 3) The metal concentration remained just about the same as the original amount at the start of the experiment. The increase at cathode was just over 1%.

The migration as well as the implication of the concentration of Zn^{2+} on the clean up of contaminated land is discussed in detail in Chapter 6.

5.2 Two Process Approach

The Two Process Approach was achieved through ‘open anode’ conditions, whereby a continuous flux of water was provided into the soil mass at the anode. Under the electrokinetic influence, the water was to flush across the contaminated soil specimen. It was hypothesised that this would facilitate the transportation of the dissolved contaminating metal cations towards the cathode end where they would be discharged with the effluent. Additionally, the aim of the water was to avoid drying up of the specimen, especially at the anode end, before treatment was completed. This section looks at laboratory test results of investigations conducted with:

- (a) two test specimens of the same length, width and continuous direct current conditions, but different vertical heights - refer to Sections 4.2.2.1 and 4.2.2.2 for the detailed test procedures,
- (b) current intermittence conditions - refer to Section 4.2.2.3, and
- (c) changing the water in draining channels aligned along the soil length – refer to Section 4.2.2.5.

For each of the these investigations, the results are presented in terms of the temporal variations in electrical current supplied to the test cell, and the spatial changes of WC and Zn^{2+} within the test specimen soil.

5.2.1 Specimen Height of 150mm with Constant Voltage Gradient

The test specimens were 400 by 200 by 150mm in length, width and height respectively and were treated at a continually applied voltage gradient of 0.5 V/cm.

(a) *Electrical Current*

Figure 5.9 shows the measured temporal electrical current for the five tests over the five week treatment period. The current of all the tests followed a simple path demonstration that the experiments were repeatable. The average initial current was 0.048A, dropping non-linearly to 0.005A by the fifth week. Just as observed in the closed anode conditions in Section 5.1, most changes in the current readings occurred during the first week of testing. However, the results in Figure 5.9 show higher respective periodic current values

than those obtained with the closed anode conditions. The reasons for the difference are given in Chapter 6.

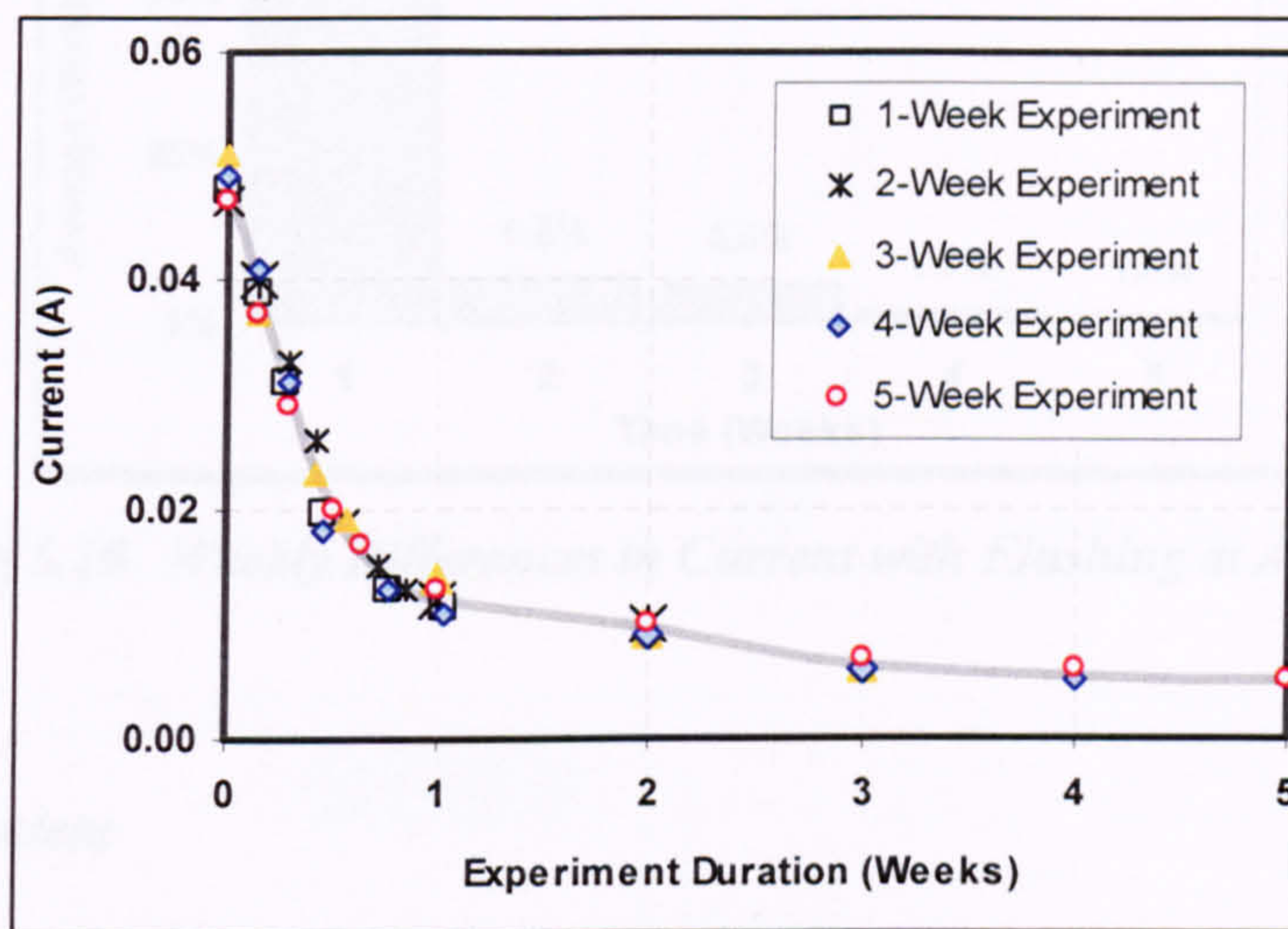


Fig 5.9 Variation of Current with Time with Flushing at Anode for $H = 150\text{mm}$

When changes in the current during the five experiments were computed in Table A5.2 (in the appendix) and presented in Figure 5.10., it was clear that:

- 1) by the end of the first week, the average current had reduced by 74.6% of the original amount. This was 10% lower than reductions obtained in the same period by specimens treated without flushing water at the anode.
- 2) for the following four weeks, the current continued to drop non-linearly. However, the drop in last three weeks of cells investigated without irrigating the anode was constant rate at 2.1%
- 3) by the end of the testing programme, the overall lowering in current was equivalent to 89.7%. Yet for the closed anode conditions, the current was zero by the fifth week.

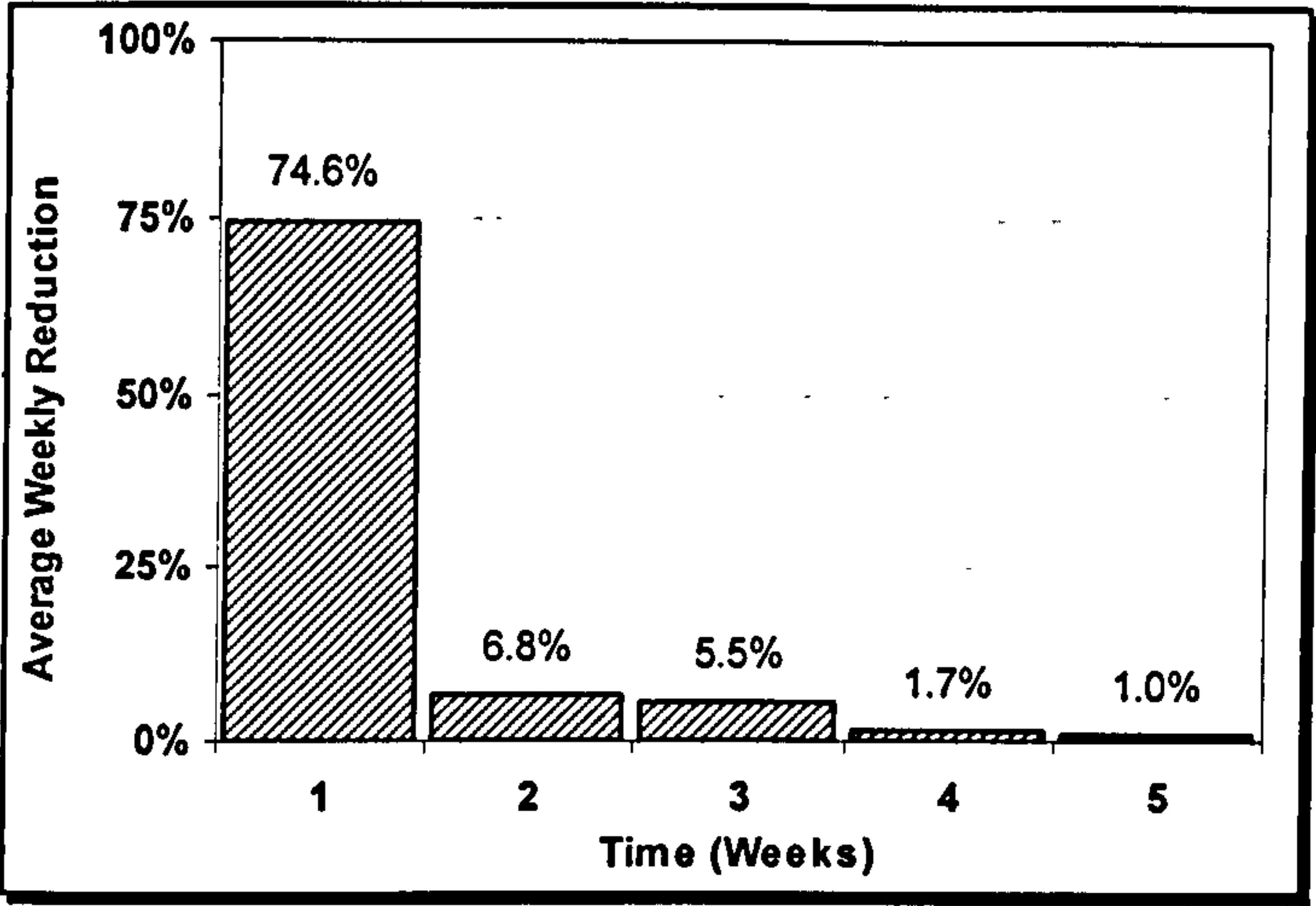


Fig 5.10 Weekly Differences in Current with Flushing at Anode

(b) Water Content

Water Content versus Normalised Distance from the Anode

The results of the WC changes in five test specimens, each conducted at different duration, are presented in Figures 5.11a, 5.11b and 5.11c for the top, middle and bottom thirds of the specimen respectively.

Generally, at the top of the cells, the highest WC was at the anode and $\frac{3}{4}L$ and lowest at $\frac{1}{2}L$. It is clear that the longer the experiment, the lower the WC values at respective positions. It was also noted that the greatest difference between profiles occurred during the first week.

In the middle third of the specimens, the general behaviour involved rapid WC decreases from anode to $\frac{1}{4}L$. The reducing slope was then gentler in the direction $\frac{1}{4}L$ and $\frac{3}{4}L$, before increasing from $\frac{3}{4}L$ to cathode. For any specific weekly plot in this region, the highest WC was experienced at the anode, followed by that at the cathode. The greatest difference between WC profiles, again, occurred during the first week of testing.

At the bottom of the cells, a more linear behaviour of WC was exhibited along the cells. It was yet again evident that the WC was highest at the anode and decreased in the direction towards the cathode for most of the weekly plots.

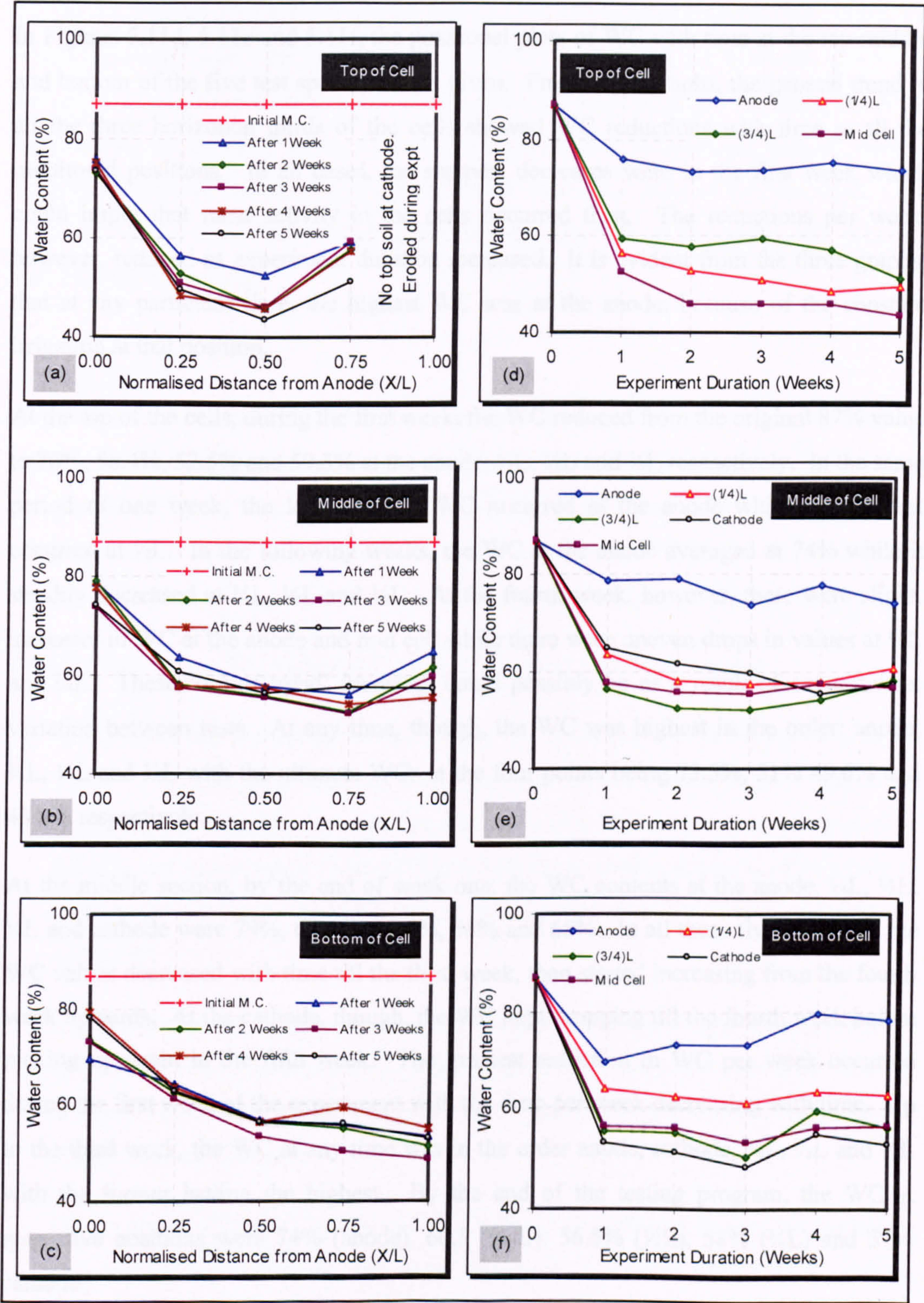


Fig 5.11 Variation of WC: along cell (a, b, c) and with Time (d, e, f) - Flushing at the Anode ($H = 150\text{mm}$)

Water Content versus Time

In Figures 5.11d, 5.11e and 5.11f, the positional plots of WC with time at the top middle and bottom of the five test specimens are given. From these graphs, the general trend in all the three horizontal thirds of the cells showed WC reductions with time at all the monitored positions. In all cases, the sharpest decreases were in the first week which could imply that most activity in the cells occurred then. The reductions per week, however, reduced as experiment duration increased. It is evident from the three graphs, that at any particular time, the highest WC was at the anode, because of the constant irrigation at that position.

At the top of the cells, during the first week, the WC reduced from the original 87% value to 76%, 56.4%, 52.5% and 59.3% at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$ and $\frac{3}{4}L$ respectively. In the same period of one week, the least drop in WC occurred at the anode while the greatest occurred at $\frac{1}{2}L$. In the following weeks, the WC at the anode averaged at 74% while it steadily decreased at $\frac{1}{4}L$, $\frac{1}{2}L$ and $\frac{3}{4}L$. At the fourth week, however, there were slight, increases in WC at the anode and mid cell while there were uneven drops in values at $\frac{1}{4}L$ and $\frac{3}{4}L$. These 'out of trend' increases could possibly be as a result of experimental variation between tests. At any time, though, the WC was highest in the order: anode, $\frac{3}{4}L$, $\frac{1}{4}L$ and $\frac{1}{2}L$ with the ultimate WCs at the four points being 73.5%, 51% 49.6% and 43.5% respectively.

At the middle section, by the end of week one, the WC contents at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$ and cathode were 79%, 63.5%, 57.5%, 56% and 65%. In all these five positions, the WC values decreased with time till the third week, then started increasing from the fourth week upwards. At the cathode, though, the WC kept dropping till the fourth week before picking up again in the fifth week. The greatest reduction in WC per week occurred during the first week of the experiment with the drop per week decreasing with time. Up to the third week, the WC at any time was in the order anode, cathode, $\frac{1}{4}L$, $\frac{1}{2}L$ and $\frac{3}{4}L$ with the former having the highest. By the end of the testing program, the WC at respective positions were 74% (anode), 60.5 ($\frac{1}{4}L$), 56.5% ($\frac{1}{2}L$), 58% ($\frac{3}{4}L$) and 57% cathode.

Like the top two thirds, the greatest decrease in WC in the bottom layer occurred during the first week. In this layer, at most times, the highest WC was in the order anode, $\frac{1}{4}L$,

$\frac{1}{2}L$, $\frac{3}{4}L$ and cathode. After one week had elapsed, the WC reduced to 69.5% 64%, 56.5%, 55.5 % and 53.5% at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$ and Cathode respectively. While the values decreased with time up to the third week at $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$ and Cathode, the WC at the anode decreased in the first week but increased in the second and remained about the same during in the third week. It was also noted that at all positions, the WC values uncharacteristically increased in the fourth week before reducing in the last week. The final WC values were 78.5%, 62.5%, 56.5%, 56% and 53% at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$ and cathode respectively.

Average Values

From Figures 5.11 a, 5.11b and 5.11c, weekly values of WC for the top, middle and bottom of the test cells were averaged (using the same method as in Section 5.1(b) above) and plotted in Figure 5.12. While from Figures 5.11d, 5.11e and 5.11f, the relationships between the experiment duration and the spatial variation in WC for the top, middle and bottom thirds of the five specimens were also averaged and plotted in Figure 5.13.

Broadly, the average WC values in Figures 5.12 and 5.13 demonstrate that:

- 1) at any time, the highest pore water in the test specimen was at the anode (Figures 5.10). And generally reduced with increased distance towards mid cell before increasing just slightly at the cathode side. This high WC at the anode was a result of the constant water supply flushing into the electrode section during the five weeks of testing. At any time, the difference in WC between the two ends of the cell was about 19%.
- 2) the periodic WC along the water flushed test specimens were higher than those of the specimens treated under closed anode conditions. The results confirm that the constant irrigation at the anode, during the electrokinetic process, accounted for the higher cell water content.
- 3) most marked difference in average longitudinal WC plots, between two sampling time periods, occurred in the first week (Figures 5.12). During that week, the greatest reduction was 30% at $\frac{1}{2}L$ and the least was 12% at the anode. Beyond the first week, the average weekly differences in WC of respective positions along the cell, was 3.5%. The longer the experiment time, the smaller the difference got and the closer

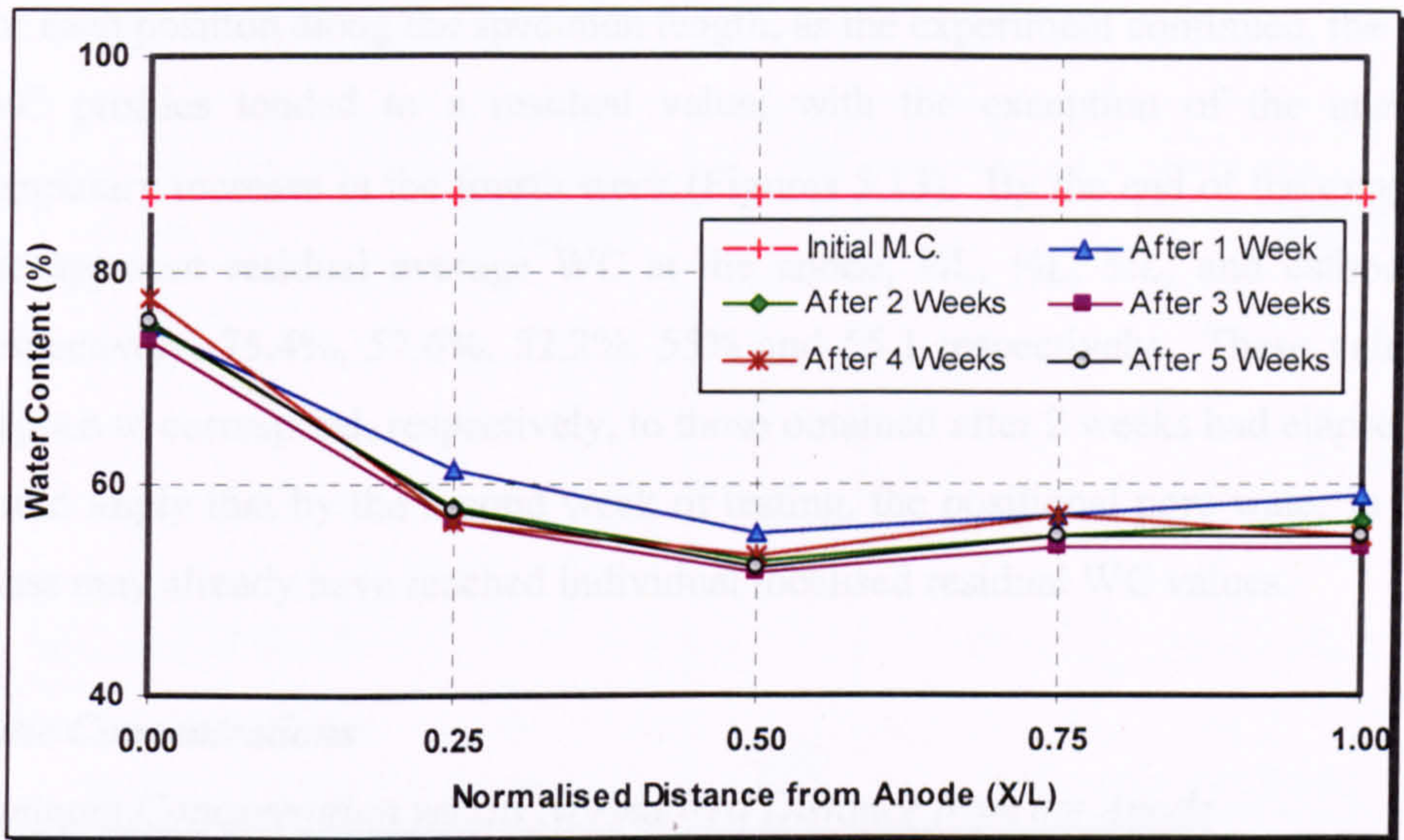


Fig 5.12 Variation of Average WC along Cell - Flushing at the Anode (H = 150mm)

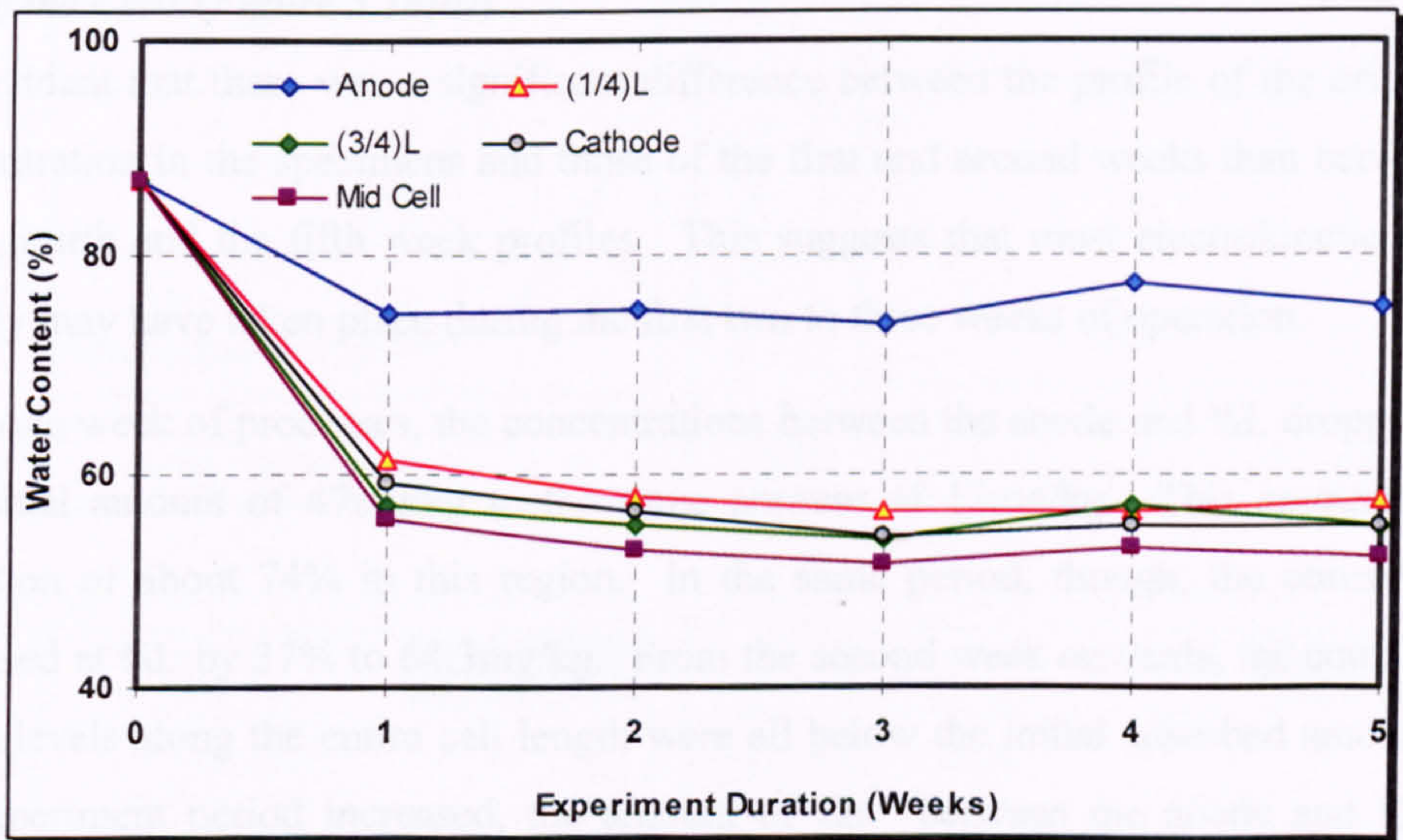


Fig 5.13 Variation of Average WC with Time - Flushing at the Anode (H = 150mm)

the profiles drew together. It was also noticed that the period after week one onwards is characterised by the decreasing WC from anode to $\frac{1}{4}L$ and an almost linear relationship from $\frac{1}{4}L$, to the cathode, (with the exception of a dip at $\frac{1}{2}L$). Therefore, at any time after one week, the average WC beyond the anode was likely to be the same irrespective of the position in the cell.

- 4) for each position along the specimen length, as the experiment continued, the average WC profiles tended to a residual value, with the exception of the unexpected temporary increase in the fourth week (Figures 5.13). By the end of the experiment, the apparent residual average WC at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$, and cathode were respectively, 75.4%, 57.6%, 52.2%, 55% and 55.1 respectively. These values also happen to correspond, respectively, to those obtained after 2 weeks had elapsed. This could imply that by the second week of testing, the positional pore water in the soil mass may already have reached individual localised residual WC values.

(c) Zinc Concentrations

Contaminant Concentration versus Normalised Distance from the Anode

The temporal variation in Zn concentration from anode to cathode, measured at the top, middle and bottom of the specimens, is shown in Figures 5.14 (a), (b) and (c).

Top of the Cells (Figure 5.14(a))

It is evident that there was a significant difference between the profile of the original Zn concentration in the specimens and those of the first and second weeks than between the third, fourth and the fifth week profiles. This suggests that most electrokinetic process activity may have taken place during the first two to three weeks of operation.

After one week of processes, the concentrations between the anode and $\frac{1}{2}L$ dropped from the initial amount of 47mg/kg to the same amount of 12mg/kg. This amounted to a reduction of about 74% in this region. In the same period, though, the concentration increased at $\frac{3}{4}L$ by 37% to 64.3mg/kg. From the second week onwards, the contaminant cation levels along the entire cell length were all below the initial adsorbed amount. As the experiment period increased, the amount of Zn^{2+} between the anode and $\frac{1}{2}L$ still remained about the same. This is depicted by the linear relationship (almost horizontal) between time and Zn^{2+} concentration in the anode half shown in Figure 5.14(a). This could suggest a possibility that the cation movement in the anode half of the cell was at the same rate in the entire duration of operations or that there was no movement at all.

Middle of the Cells (Figure 5.14(b))

In the first week the metal concentration reduced between the anode and $\frac{1}{2}L$ whilst it increased at the cathode and $\frac{3}{4}L$. In this period, the lowest concentration was 12.5mg/kg measured at the anode and $\frac{1}{2}L$. This concentration was nearly the same as the one

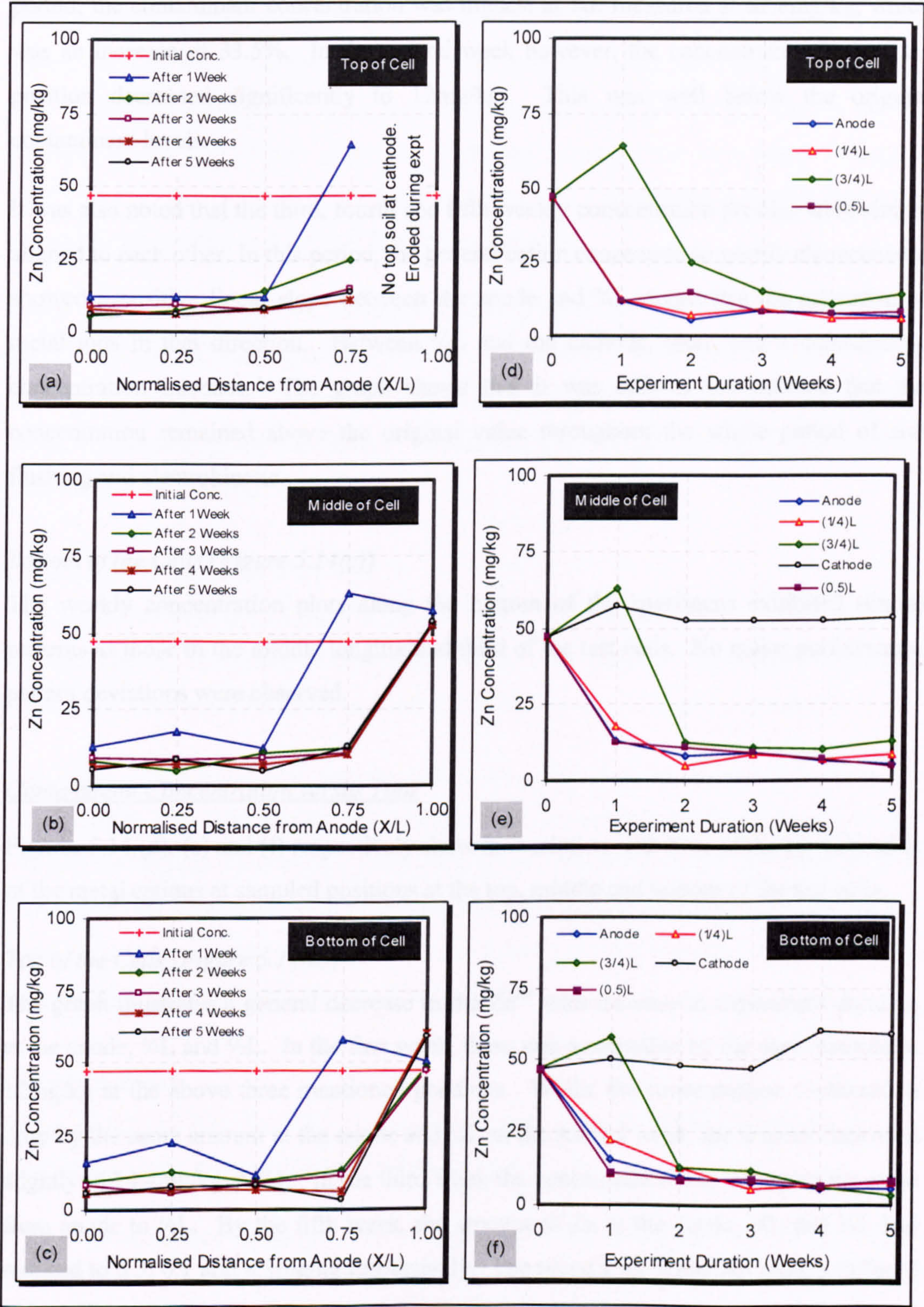


Fig 5.14 Variation of Zinc Concentration (a, b, c) along cell and (d, e, f) with Time - with Flushing at the Anode ($H = 150\text{mm}$)

determined in the respective positions of top third of the cells. In the same reference period, the contaminant concentration was highest at $\frac{3}{4}L$ measured at 62.8mg/kg, which was an increase of 33.5%. In the second week however, the concentration in the later position decreased significantly to 12mg/kg. This was well below the original contaminant levels.

It was also noted that the third, fourth and fifth weekly concentration profiles were almost aligned to each other. In this period, the general cation concentration profile characteristic showed a positive linear slope between the anode and $\frac{3}{4}L$ suggesting the migration of metal ions in that direction. Between $\frac{3}{4}L$ and the cathode, there was a considerable concentration increase. The graph shows that it was only at the cathode that the concentration remained above the original value throughout the whole period of soil flushing and electrokinetic.

Bottom of the Cells (Figure 5.14(c))

The weekly concentration plots along the bottom of the specimens exhibited similar patterns as those in the middle longitudinal third of the test cells. No major performance pattern deviations were observed.

Contaminant Concentration versus Time

Figures 5.14 (d), (e) and (f) respectively show the variation with time of the concentration of the metal cations at sampled positions at the top, middle and bottom of the test cells.

Top of the Cells (Figure 5.14(d))

The graph illustrates a general decrease in the Zn^{2+} with increase in experiment duration at the anode, $\frac{1}{4}L$ and $\frac{1}{2}L$. In the first week, there was a reduction by the same amount to 12mg/kg at the above three mentioned positions. Whilst the concentration continued to drop by the same amount at the anode and $\frac{1}{4}L$ in the second week, the amount increased slightly to 14.4mg/kg at $\frac{1}{2}L$. In the third week the concentration was yet again the same from anode to $\frac{1}{2}L$. By the fifth week, the amount of Zn at the anode, $\frac{1}{4}L$ and $\frac{1}{2}L$ had reduced to 6.3, 6.1 and 8.3mg/kg respectively. The metal ions behaviour pattern differed at $\frac{3}{4}L$. The concentration first increased in week one to 64.3mg/kg before falling to 25 and 15mg/kg at the second and third week respectively. From the third week the concentration increased again to 13.9mg by the end of the experiment.

Middle of the Cells (Figure 5.14(e))

The general trend was a reduction in contaminant levels with increase in time at the anode, $\frac{1}{4}L$ and $\frac{1}{2}L$. The decrease in the three positions in the first week was 12.8, 17.3 and 12.4mg/kg respectively. The greatest percentage reduction in this half of the cell occurred during this period. After one week had elapsed, there were small differential Zn^{2+} concentration levels in this half of the specimen. The ultimate contaminating metal concentrations were 5.4, 8.3 and 4.8mg/kg respectively.

In the cathode half of the cell, the metal concentration levels increased in week one to 63 and 57mg/kg at $\frac{3}{4}L$ and cathode respectively. In the second week, there was a drop at $\frac{3}{4}L$ to 12mg/kg while the pollutant levels stabilised at 52.5mg/kg at the cathode till the fifth week. Consequently, the contaminant concentration at the cathode was higher than the original amount by 11%.

Bottom of the Cells (Figure 5.14(f))

The trends followed by the plots at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$ and $\frac{3}{4}L$ were similar to those of the layer above. The concentrations of the residual adsorbed Zn^{2+} on the clay particles at the four sampled positions referred to were 5.5, 7.8, 8.3 and 3.2mg/kg respectively.

The trend, however, at the cathode was unique. By the end of the first week, the concentration had increased by just 4mg/kg. The concentration then decreased until it reached the original value by the third week before increasing again. By the end of the experiment, the concentration at this position was 59mg/kg. This could suggest that the metal ions were probably coming out of solution and precipitating at bottom of the cathode area. This is further discussed in Chapter 6.

Average Values

From Figure 5.14(a), (b), and (c) above, average weekly spatial variations in Zn^{2+} concentrations were computed and plotted in Figure 5.15.

It is observed, from the graph, that by the end of the first week the average cation concentration in the anode half (from the anode to $\frac{1}{2}L$) dropped while it increased from $\frac{3}{4}L$ to cathode. In this period, the average drop between the anode and $\frac{1}{2}L$ was 69.6% while the average increase between $\frac{3}{4}L$ and the cathode was 23%. By the second week,

the major changes occurred at the $\frac{3}{4}L$ where the average concentration dropped from 61.6mg/kg to 16.6mg/kg.

The results also show that from the second week onwards, a linear relationship in metal ions concentration had been established between the anode and $\frac{3}{4}L$. The longer the experiment duration, the smaller the concentration gradient differences between individual positions from the anode to $\frac{3}{4}L$. It is evident by the third to the fifth weekly plots that, the respective metal ion concentration gradients were actually drawing closer to zero. This implied that the metal ions concentration levels between the anode and $\frac{3}{4}L$ could have been tending towards the same residual value. This also could infer that minimal ions were being washed away from this region of the cell from the third week onwards or that probably there was no net movement of ions at all. The concentration profiles, though, showed that there was still more activity at the cathode area where increases were still being registered from the third week. In this same period, there were steeper concentration gradients between $\frac{3}{4}L$ and the cathode. The steeper gradient remained until the end of the experiment.

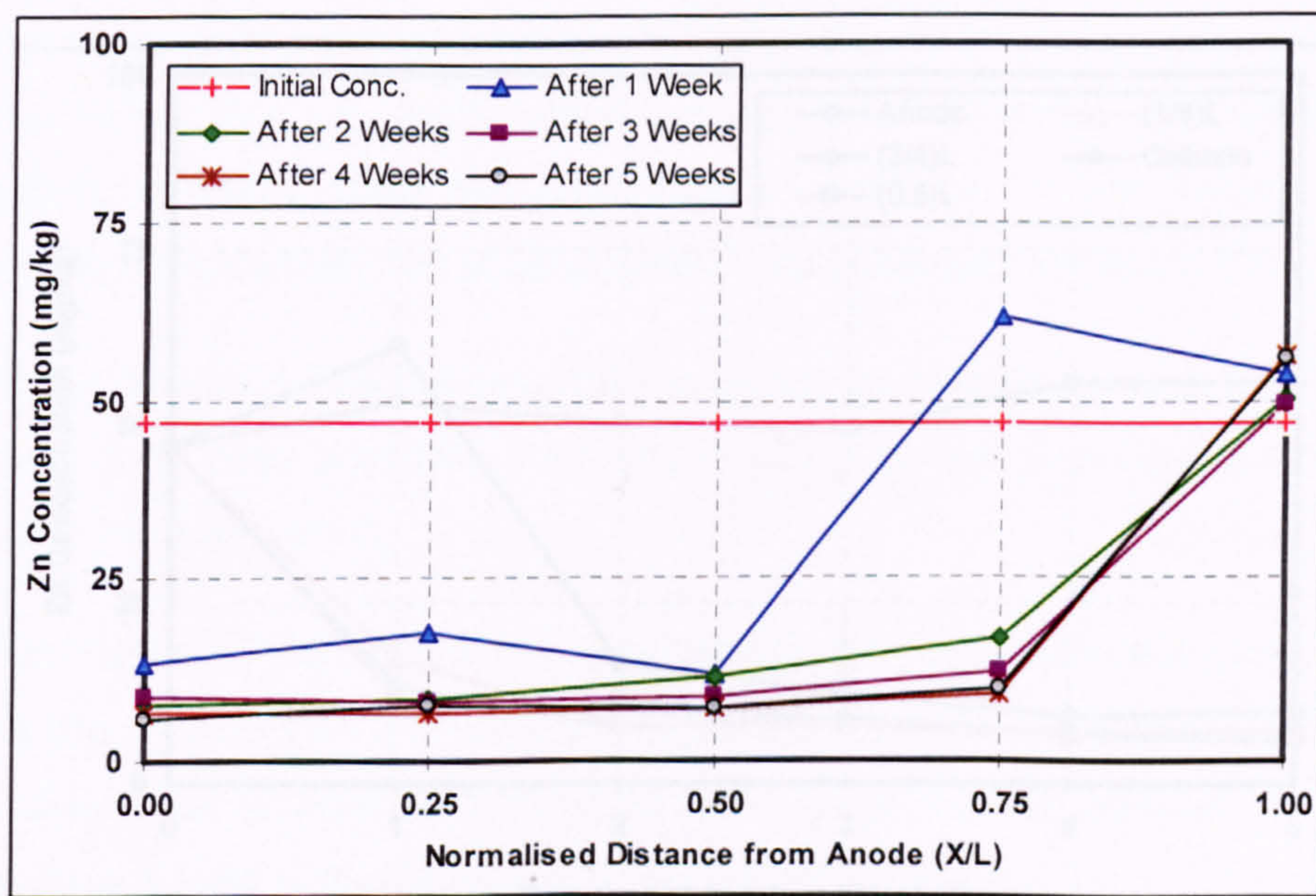


Fig 5.15 Variation of Average Zinc Concentration along Cell - Flushing at the Anode ($H = 150\text{mm}$)

In Figure 5.16 below, the graph of the average behaviour of the metal, at specific positions in the cell, versus the experiment duration is presented. The values in this figure were calculated from Figure 5.14(d), (e), and (f).

The graph shows that during the first week, the decrease in average contaminant values in the anode half of the cell was matched by increases at the cathode and $\frac{3}{4}L$. In this first week, the highest contaminant extraction was attained at mid cell and the highest accumulation occurred at $\frac{3}{4}L$. By the end of the second week, there was a major metal removal at $\frac{3}{4}L$ position. The difference between the one and two week average values at this position producing a net removal of Zn^{2+} of 45mg/kg. This made the concentration in this position well below the value at the start of the experiment, but was within the contaminant levels as those from the anode to $\frac{1}{2}L$.

From the third, fourth and fifth weeks, there was only a minimal reduction in the metal ion concentration between the anode and $\frac{3}{4}L$. In this reporting period, the average weekly differences between the respective positions of the cell were within $\pm 3\text{mg/kg}$. It was also observed that at each of the third, and fourth weeks duration results, the concentrations especially in the anode half of the cell, approximated to the same value.

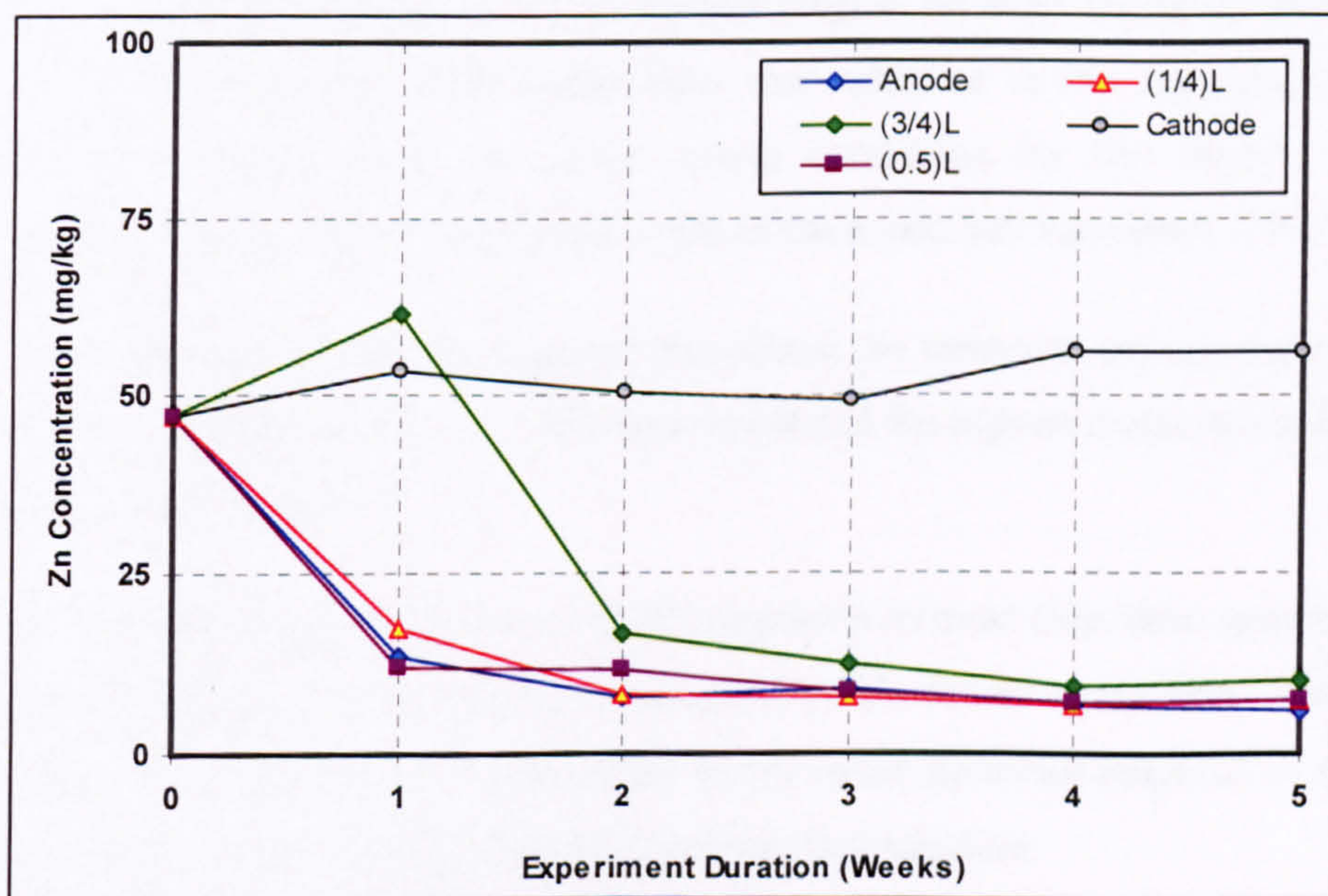


Fig 5.16 Variation of Average Zinc Concentration with Time - Flushing with Water ($H = 150\text{mm}$)

At the cathode end, there was a reduction from the average of 53.6mg/kg by the end of the first week to 50.2mg/kg after two weeks had elapsed. This concentration reduced slightly in the third week to 49.4mg/kg before increasing to 56.3 and 56.1mg/kg in the fourth and fifth weeks respectively. It is clear that the average results predict that the metal concentration at this extreme end of the cell did not fall below the original. The probable reason for this, as pointed out earlier, could have been metal precipitation especially at the bottom of the electrode area. The detailed discussion, though, is presented in Chapter 6.

Between the fourth and fifth weeks, the plots show that respective positional difference in concentration values were negligible. It is possible that by the fourth week of the experiment the maximum amounts of the contaminants that could be removed, under these testing conditions, had been reached.

The averages of the metal cations still remaining along the soil length at the end of the five weeks of treatment were read off from Figure 5.16 and presented in Table 5.4 below. The respective values were compared with the Zn^{2+} present in the soil mass at the start of the investigation to determine the net change in cation concentrations at each of the five sampled regions. From the comparison, also presented in Table 5.2, it is evident that:

- 1) The contaminant reduced in the anode half (region between the anode and $\frac{1}{2}L$) by over 84%. This was much higher than was achieved in the same region of the specimens treated under the closed anode conditions for five weeks. In that investigation, the reduction in metal levels in the anode half was nearly 75%.
- 2) The anode area, which was irrigated throughout the treatment period, experienced a contaminant removal of 88%. This area registered the highest metal reduction by the end of the investigation.
- 3) The clean up operation produced metal reductions in more than three quarters of the test cell. Specifically, at $\frac{3}{4}L$, the contaminant levels decreased by 79%. This was in contrast to an increase of 152% of the heavy metal pollutant recorded in the same region at the end of the closed anode treatment investigation.
- 4) At the cathode, however, the final Zn^{2+} concentration was above the initial amount by 20%. This was the only section of the cell where the metal levels were higher than

those at the start of the processes. Concentrating the contaminant at one end of the cell is advantageous to the treatment operation as explained in Chapter 6.

- 5) The combined treatment operation of soil flushing and electrokinetics, therefore, resulted in better clean up results as noted in 1) to 3) above.

The implications and the full discussions of all the above are presented in Chapter 6.

Table 5.2 Average Zn Concentration after 5 Weeks Had Elapsed: Flushing at Anode (H = 150mm)

Position along Cell	Zinc Concentration after 5 Weeks (mg/kg)	Concentration Increase (+) / Decrease (-) (mg/kg)	Percentage Changes (+/-) (%)
Anode	5.7	-41.2	-88
¼L	7.4	-39.5	-84
Mid Cell	7.1	-39.8	-85
¾L	9.9	-37	-79
Cathode	56.1	9.2	20

5.2.2 Specimen Height of 300mm with Constant Voltage Gradient

In this investigation, the test specimens were double the height of those in Section 5.2.1 while the rest of the dimensions were maintained. Like in the previous investigations, a constant voltage gradient of 0.5 V/cm was maintained across the soil specimens. The purpose of these experiments was to compare results with those obtained in Section 5.2.1 and consequently determine the effect of depth on the treatment process. As mentioned in Section 4.2.3, in order to minimise the effect of the boundary conditions, the samples at the top (top of the cell was open to the atmosphere so that the generated gases could freely escape) and bottom of the cell were sampled approximately 1 cm away from the top and bottom surfaces respectively.

(a) Electrical Current

In Figure 5.17 below, the relationship between the electrical current in the respective test cells and experiment duration over the five week testing period is presented. The figure illustrates that there was consistency among results from all five test cells which displayed repeatability. The average initial current at the start of experiment was 0.097A, but reduced in a non-linear relationship to 0.007A by the end of the fifth week of treatment. These results show a similar trend with those obtained from experiments conducted on 150mm deep specimens (Figure 5.9). However, further comparisons shows that at any particular test duration, the electrical currents to respective test cells were generally double those of the half sized test samples. This established that doubling the sample height while keeping all other parameters unchanged, resulted in the doubling of the periodic electrical current flowing into the test cell. The significance of this observation is detailed in Chapter 6.

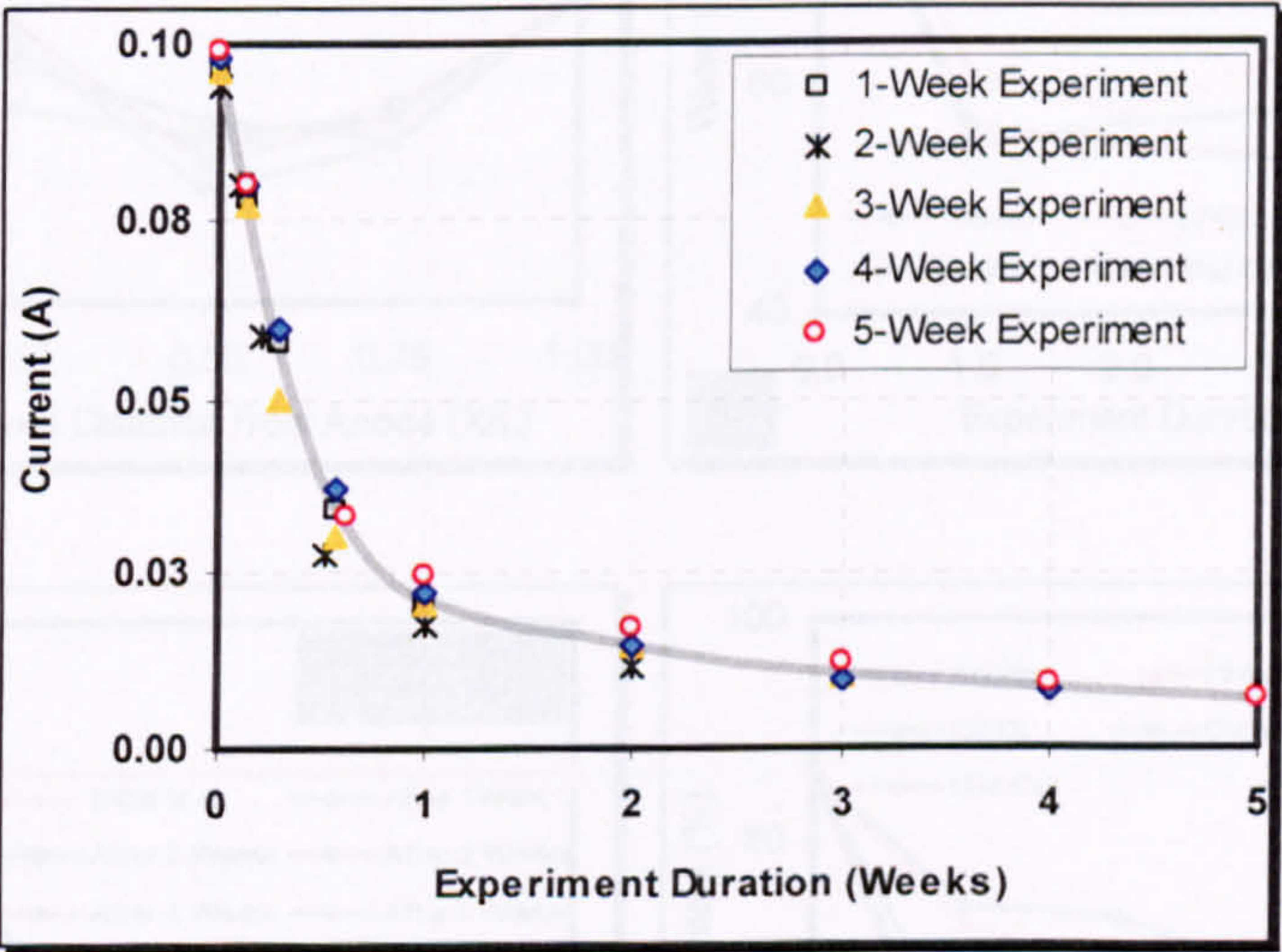


Fig 5.17 Variation of Current with Time with Flushing at Anode for H = 300mm

(b) Water Content

Water Content versus Normalised Distance from the Anode

The graphs in Figure 5.18 show the results of the periodic WC changes along the three horizontal specimen thirds.

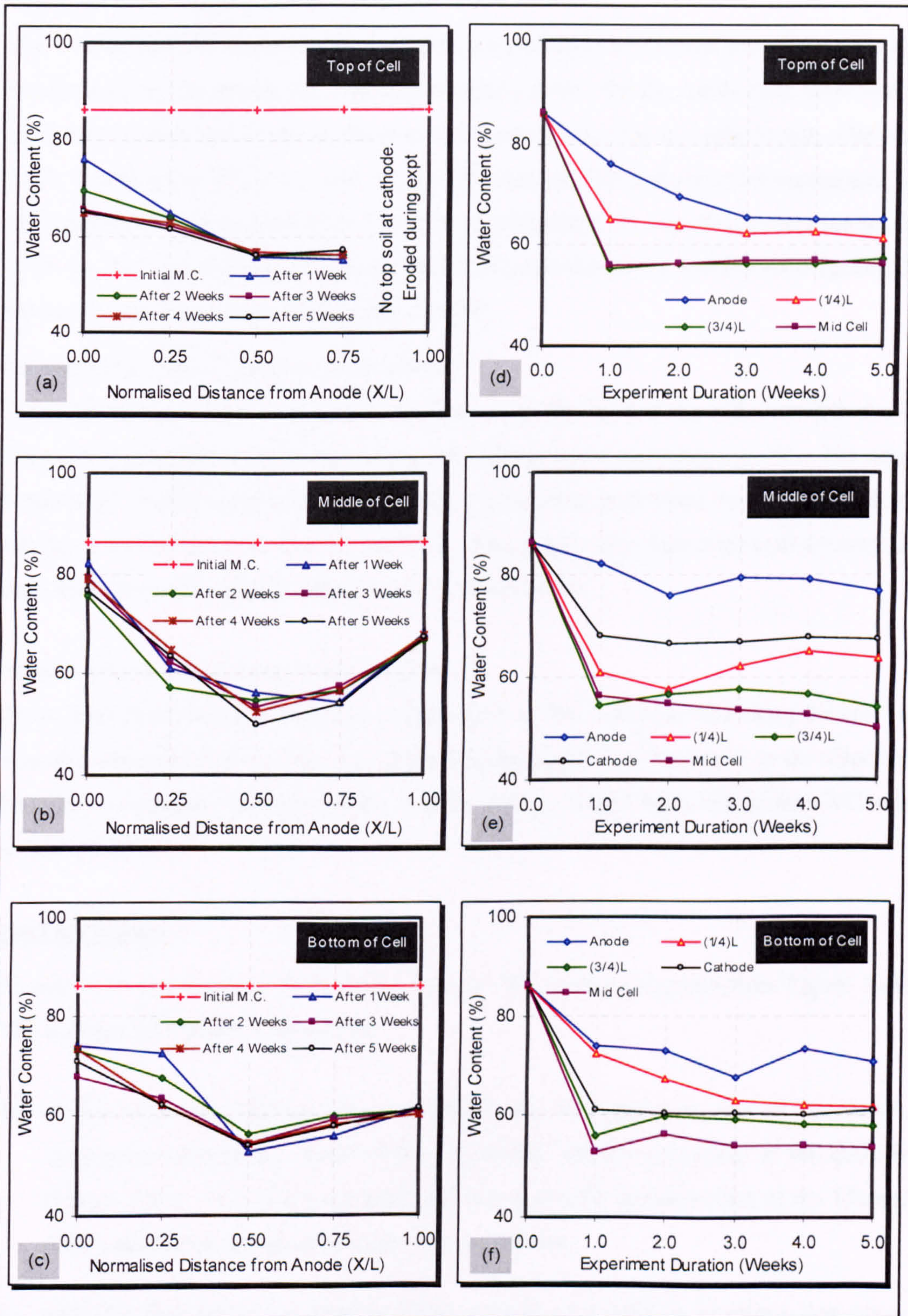


Fig 5.18 Variation of WC: (a, b, c) along cell and (d, e, f) with Time - Flushing at the Anode ($H = 300\text{mm}$)

Top of the Cells (Figures 5.18(a) and (d))

The five weekly WC behaviour characteristics appeared to be divided into two halves; the anode (between the anode and $\frac{1}{2}L$) and cathode halves. On the anode side, there was a continuous reduction in value in the direction anode to $\frac{1}{2}L$. On the cathode side, after one week of testing the WC at $\frac{1}{2}L$ and $\frac{3}{4}L$ was the same at 56% and remained unchanged till the experiment was stopped after 5 weeks. Additionally, as expected, at any particular time, the WC was higher in the anode half of the cell due to the continuous irrigation of the anode with water from the flushing chamber.

Middle of the Cells (Figures 5.18(b) and (e))

The general trend of the weekly WC profiles, along this third of the cell, was that of a U shape; with the highest WC at the anode and cathode and lowest values at $\frac{1}{2}L$. The same patterns of results were exhibited by the experiments performed on a 150mm high specimen sample (refer to Section 5.2.1(b)). The graphs also show a general decrease in pore water for each position with increase in test duration.

Bottom of the Cells (Figures 5.18(c) and (f))

At the bottom of the cell, a more linear behaviour of WC was observed along the cell. It was also observed that the WC was highest at the anode and decreased in the direction towards the cathode for most of the weekly plots. At any time, the lowest WC was measured at $\frac{1}{2}L$.

Average Values

Figures 5.19 and Figure 5.20 show the average WC results computed from Figure 5.18. The average WC results indicate that:

- 1) at any time, the highest water content in the test specimen was at the anode, decreasing towards the centre of the cell before slightly increasing at the cathode (Figure 5.19). This WC trend exhibited was generally similar to that of the 150mm thick samples treated under the same test conditions.
- 2) after the first week, the residual water content at respective positions was being established. This is well illustrated in Figure 5.18 where it is observed that from the second week, the average WC during the cleaning operation averaged about; 72%, 62.5%, 54.5%, 57% and 64% at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$, cathode respectively.

Residual WC values were also established in the same period for the 150mm high specimen samples.

- 3) the largest changes in weekly WC values occurred in the first week of experiments just like in all previous investigations of both closed and open anode test conditions.
- 4) The ultimate average WC at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$, cathode were respectively; 71%, 62.5%, 53.5%, 56.5% and 64%. The values were respectively similar with

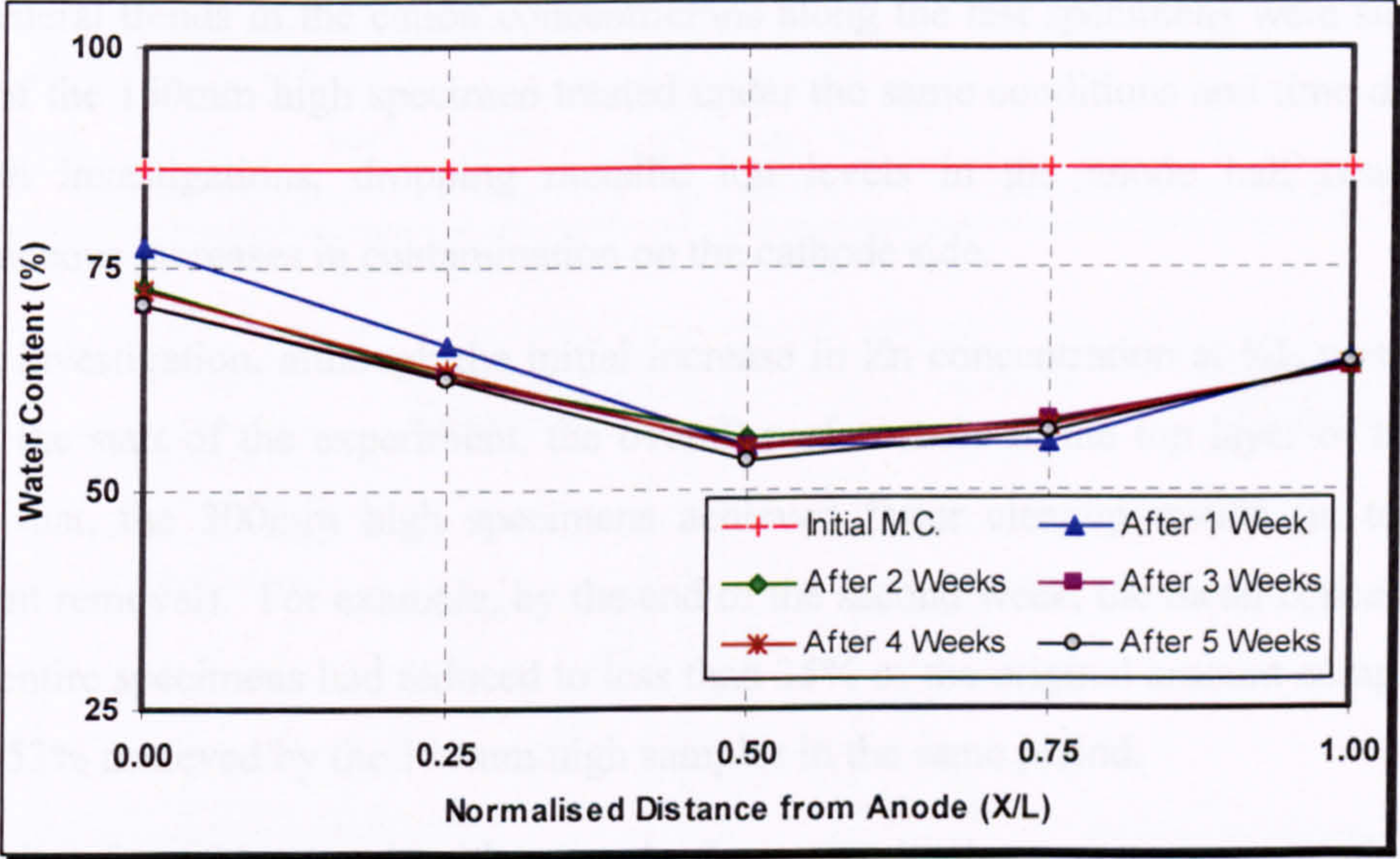


Fig 5.19 Variation of Average WC along Cell - Flushing at the Anode (H = 300mm)

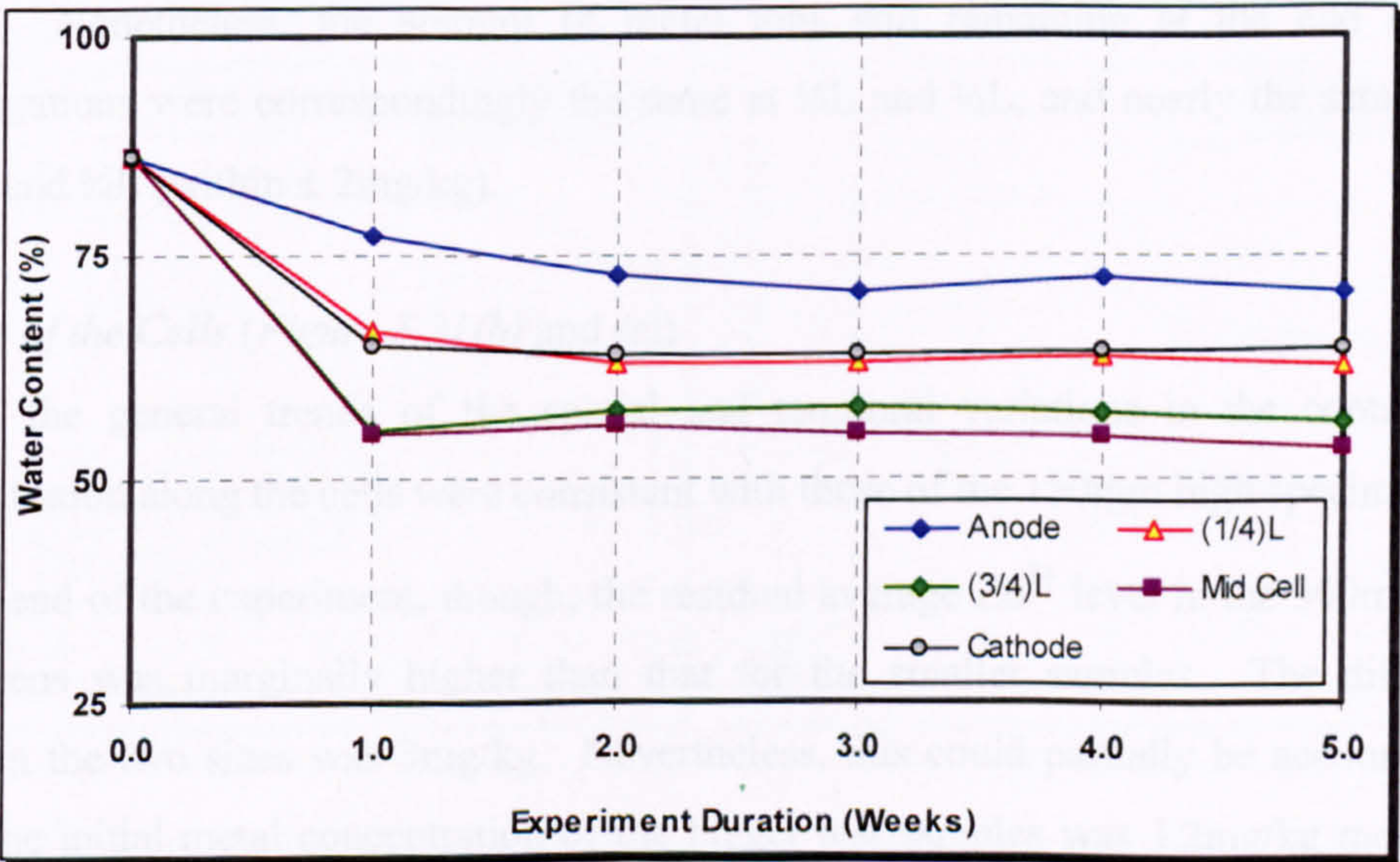


Fig 5.20 Variation of Average WC with Time - Flushing at the Anode (H = 300mm)

those obtained at the end of five weeks testing of soil specimens which were half the size.

(c) Zinc Concentrations

The graphs in Figure 5.21 present the temporal and spatial variations in the amount of contaminating cation in the test soil specimens over the respective treatment durations.

Top of the Cells (Figure 5.21(a) and (d))

The general trends in the cation concentrations along the test specimens were similar to those of the 150mm high specimen treated under the same conditions and time duration. In both investigations, dropping metallic ion levels in the anode half resulted in simultaneous increases in contamination on the cathode side.

In this investigation, although the initial increase in Zn concentration at $\frac{3}{4}L$ was double that at the start of the experiment, the overall performance in the top layer of the cells shows that, the 300mm high specimens achieved faster cleanup results (in terms of pollutant removal). For example, by the end of the second week, the metal concentration in the entire specimens had reduced to less than 35% of the original amount compared to nearly 53% achieved by the 150mm high samples in the same period.

In addition, from the second week onwards, the contaminating cations concentration at all positions along the cells continued to reduce even further with time, unlike the half sized samples which still recorded rises at certain sections of the cells from the third week onwards. Nonetheless, the amount of metal ions still remaining at the end of both investigations were correspondingly the same at $\frac{1}{4}L$ and $\frac{1}{2}L$, and nearly the same at the anode and $\frac{3}{4}L$ (within $\pm 2\text{mg/kg}$).

Middle of the Cells (Figure 5.21(b) and (e))

Again, the general trends of the spatial and temporal variations in the contaminant concentration along the cells were consistent with those of the 150mm high specimens.

At the end of the experiment, though, the residual average Zn^{2+} level in the 300mm high specimens was marginally higher than that for the smaller samples. The difference between the two sizes was 3mg/kg . Nevertheless, this could partially be accounted for since the initial metal concentration of the bigger test samples was 3.2mg/kg more than that of the smaller samples.

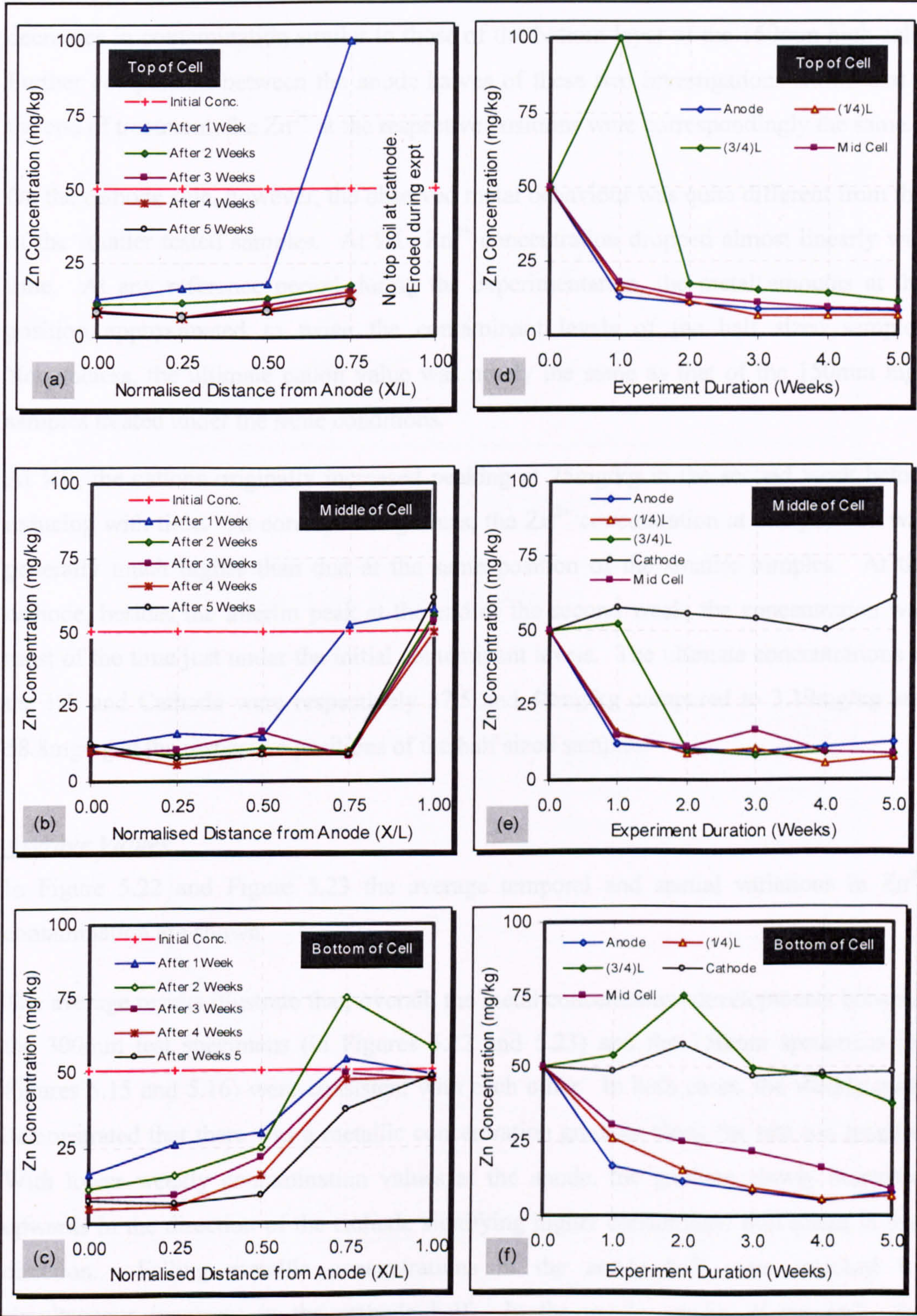


Fig 5.21 Variation of Zinc Concentration (a, b, c) along cell and (d, e, f) with Time - with Flushing at the Anode ($H = 300\text{mm}$)

Bottom of the Cells (Figure 5.21(c) and (f))

In this cell layer, only the anode side (from the anode to $\frac{1}{2}L$) experienced temporal decreases in contamination similar to those of the bottom layer of the 150mm high cells. Further comparison between the anode halves of these two investigations shows that at the end of treatment, the Zn^{2+} at the respective positions were correspondingly the same.

On the cathode side, however, the observed metal behaviour was quite different from that of the smaller tested samples. At $\frac{1}{2}L$, Zn^{2+} concentration dropped almost linearly with time. At any reference period during the experimentation, the metal amounts at this position approximated to twice the contaminant levels of the half sized samples. Nonetheless, the ultimate cation value was nearly the same as that of the 150mm high samples treated under the same conditions.

At $\frac{3}{4}L$, the cations originally increased peaking at 75mg/kg in the second week before reducing with time. At corresponding times, the Zn^{2+} concentration at this position was generally much higher than that at the same position of the smaller samples. At the cathode, besides the interim peak at the end of the second week, the concentration was most of the time just under the initial contaminant levels. The ultimate concentrations at the $\frac{3}{4}L$ and Cathode were respectively 37.5 and 48mg/kg compared to 3.19mg/kg and 58.8mg/kg at the respective positions of the half sized samples.

Average Values

In Figure 5.22 and Figure 5.23 the average temporal and spatial variations in Zn^{2+} contamination are shown.

The average results illustrate that, overall, the metal concentration developments between the 300mm test specimens (in Figures 5.22 and 5.23) and the 150mm specimens (in Figures 5.15 and 5.16) were consistent with each other. In both cases, the weekly plots demonstrated that there was a metallic concentration gradient along the test soil lengths. With lower weekly contamination values at the anode, the gradient slowly increased upwards in the direction of the cathode signifying higher contaminant movement in that direction. Falling metallic concentrations in the anode half were matched by simultaneous increases in the cathode half. In the anode section of the cells, the concentration consistently continued to fall until the close of the testing in both investigations.

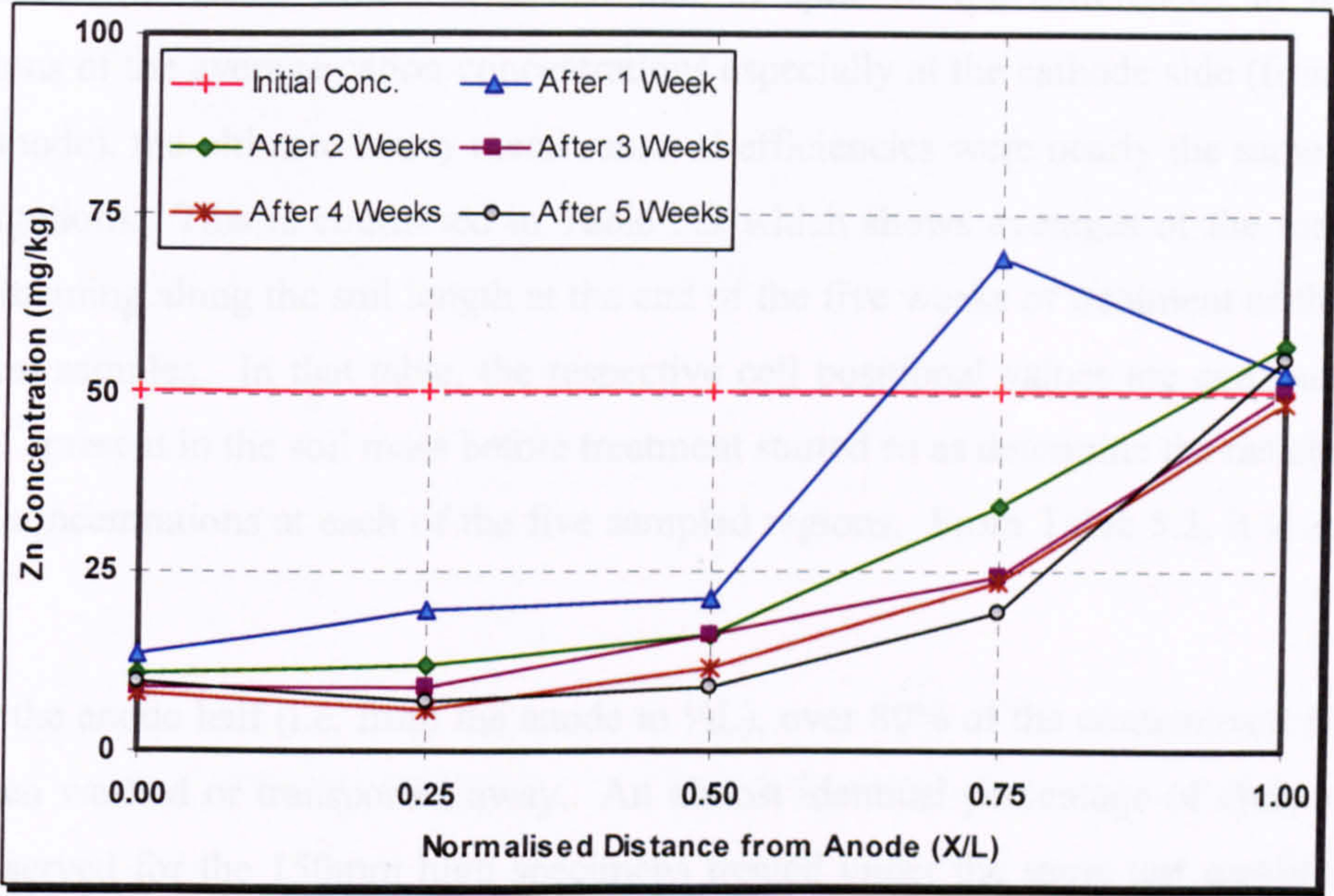


Fig 5.22 Variation of Average Zinc Concentration along Cell - Flushing at the Anode ($H = 300\text{mm}$)

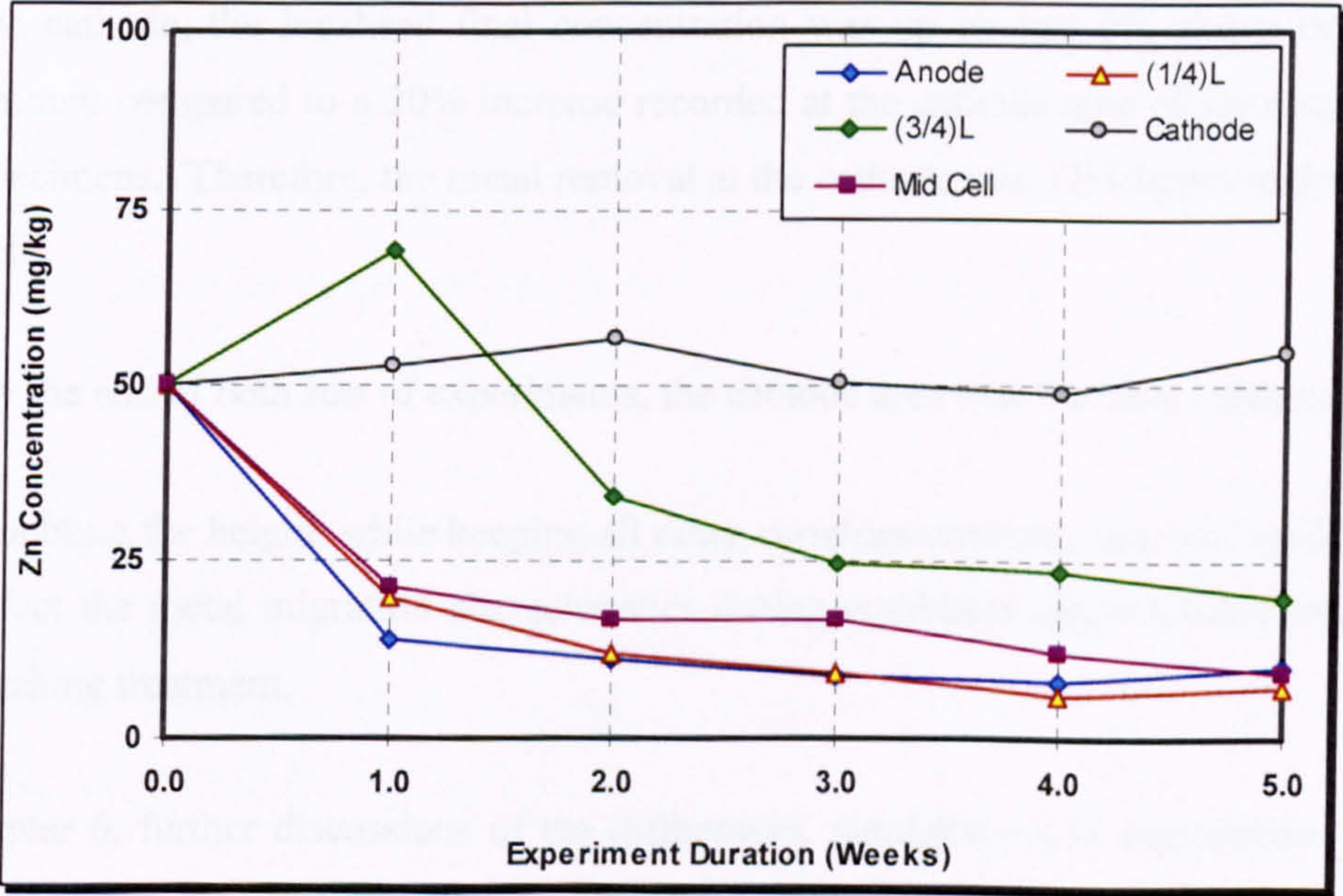


Fig 5.23 Variation of Average Zinc Concentration with Time - Flushing with Water ($H = 300\text{mm}$)

The treatment results further establish that in spite of the differences in temporal variations of the average cation concentrations especially at the cathode side (from $\frac{1}{2}L$ to the cathode), the ultimate heavy metal removal efficiencies were nearly the same in both investigations. This is confirmed in Table 5.3 which shows averages of the metal ions still remaining along the soil length at the end of the five weeks of treatment of the 300mm high test samples. In that table, the respective cell positional values are compared with the Zn^{2+} present in the soil mass before treatment started so as to determine the net change in cation concentrations at each of the five sampled regions. From Table 5.3, it is apparent that:

- 1) In the anode half (i.e. from the anode to $\frac{1}{2}L$), over 80% of the contaminant ions had been washed or transported away. An almost identical percentage of clean up was observed for the 150mm high specimens treated under the same test conditions for five weeks (refer to Table 5.2).
- 2) At $\frac{3}{4}L$, the ultimate achieved metal removal was 62%. This was nearly 15% lower than was observed in the same region of the 150mm high specimens. However, at the cathode, the localised final concentration was up by just 9% above the initial amount compared to a 20% increase recorded at the cathode area of the smaller test specimens. Therefore, the metal removal at the cathode was 11% better in the bigger cell.
- 3) By the end of both sets of experiments, the cathode area was the most contaminated.
- 4) Doubling the height, while keeping all other variables constant, may not significantly affect the metal migration characteristics during combined electrokinetic and water flushing treatment.

In Chapter 6, further discussions of the differences, similarities and implications of the two investigations, in terms of the metal contaminant movement / extraction during treatment are presented.

Table 5.3 Average Zinc Concentration after 5 Weeks Had Elapsed: Flushing at Anode (H = 300mm)

Position along Cell	Zinc Concentration after 5 Weeks (mg/kg)	Concentration Increase (+) / Decrease (-) (mg/kg)	Percentage Changes (+/-) (%)
Anode	9.6	-40.5	-81
¼L	6.9	-43.2	-86
Mid Cell	8.9	-41.2	-82
¾L	19.3	-30.8	-62
Cathode	54.6	4.5	9

5.2.3 Intermittent Current

In this investigation, all the test specimens used were similar in dimensions to those in Section 5.2.1. In all tests, though, current intermittence was exercised using an on/off switch. The current intermittence intervals of 24 hours on and 24 hours off were used with the same voltage gradient of 0.5 V/cm being applied across the soil specimens. In addition, the metal contaminated specimens were treated for ten weeks based on the fact that the actual time these cells were run with the electrical current switched on was equivalent to 5 weeks as was the case in the specimens treated with uninterrupted power supply.

The purpose of this investigation was to determine if the benefit of reduced power consumption (through periodic current interruption) would also result in the efficiency of treatment – in terms of metal removal - being significantly improved. The hypothesis of how this was expected to work is already presented in Section 4.2.2.3. The results of these tests are presented in this section.

(a) Electrical Current

In Figure 5.24 below, the changes in the temporal current supplied to the four test cells are shown. The results from these cells treated for different test times depict identical patterns with evidence of repeatability, and show a similar trend with the results of

experiments conducted with the same sized soil specimens treated with continuous direct current (DC) supply (refer to Figure 5.9). Further comparison of the average respective weekly measured current values between these two investigations shows that the values were within $\pm 0.002\text{A}$ of each other. In Chapter 6, these observations are analysed further and their effect on the removal of the metal contaminants discussed.

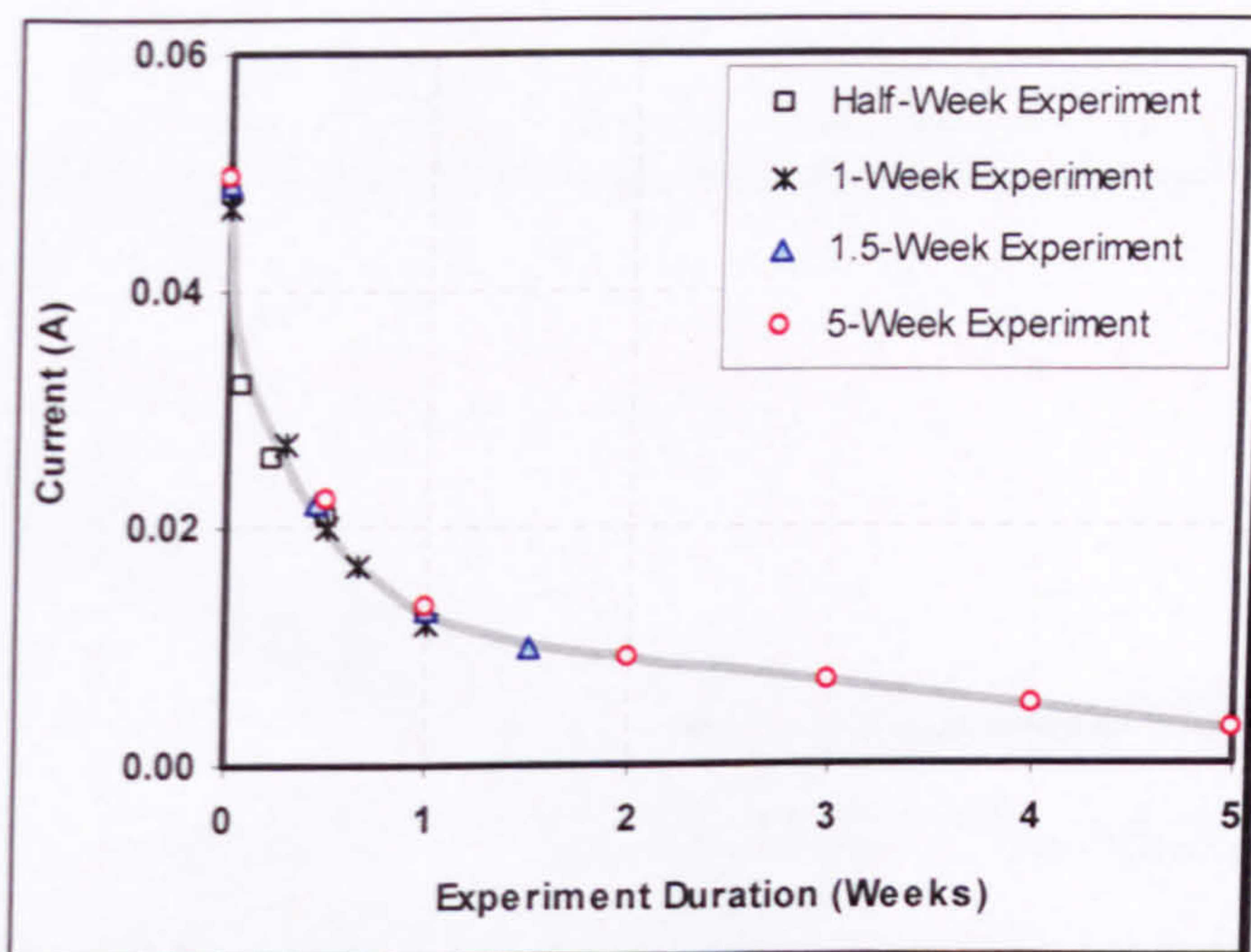


Fig 5.24 Variation of Current with Time (Based on actual time the current was switched on)

(b) Water Content

Figure 5.25 shows the average WC gradients along the cell lengths. The averages were computed from Figure A5.1 in the appendix which shows the temporal and spatial variations in WC content for the top, middle and bottom thirds of the test specimens treated with the intermittent electrical current. It was observed in Figure 5.25 that for any weekly WC profile, the highest average water content values were expectedly at the anode. For any particular plot, the WC decreased towards the centre of the cells before increasing in the direction of the cathode. It was also noted that major differences between respective profiles occurred between the start of the experiment and the end of week one. These occurrences were consistent with the observations made in the earlier test results presented in Sections 5.2.1 and 5.2.2 for investigations conducted with non stop direct currents.

In Figure 5.26 the cells positional changes in average WC with time were presented. In general, the plot shows that the average WC reduced with time at all the five sampled positions of the cells. This behaviour was a deviation from that of specimens treated with uninterrupted electrical current where the respective cell water content values had reached to the residual values by the end of the second week of treated.

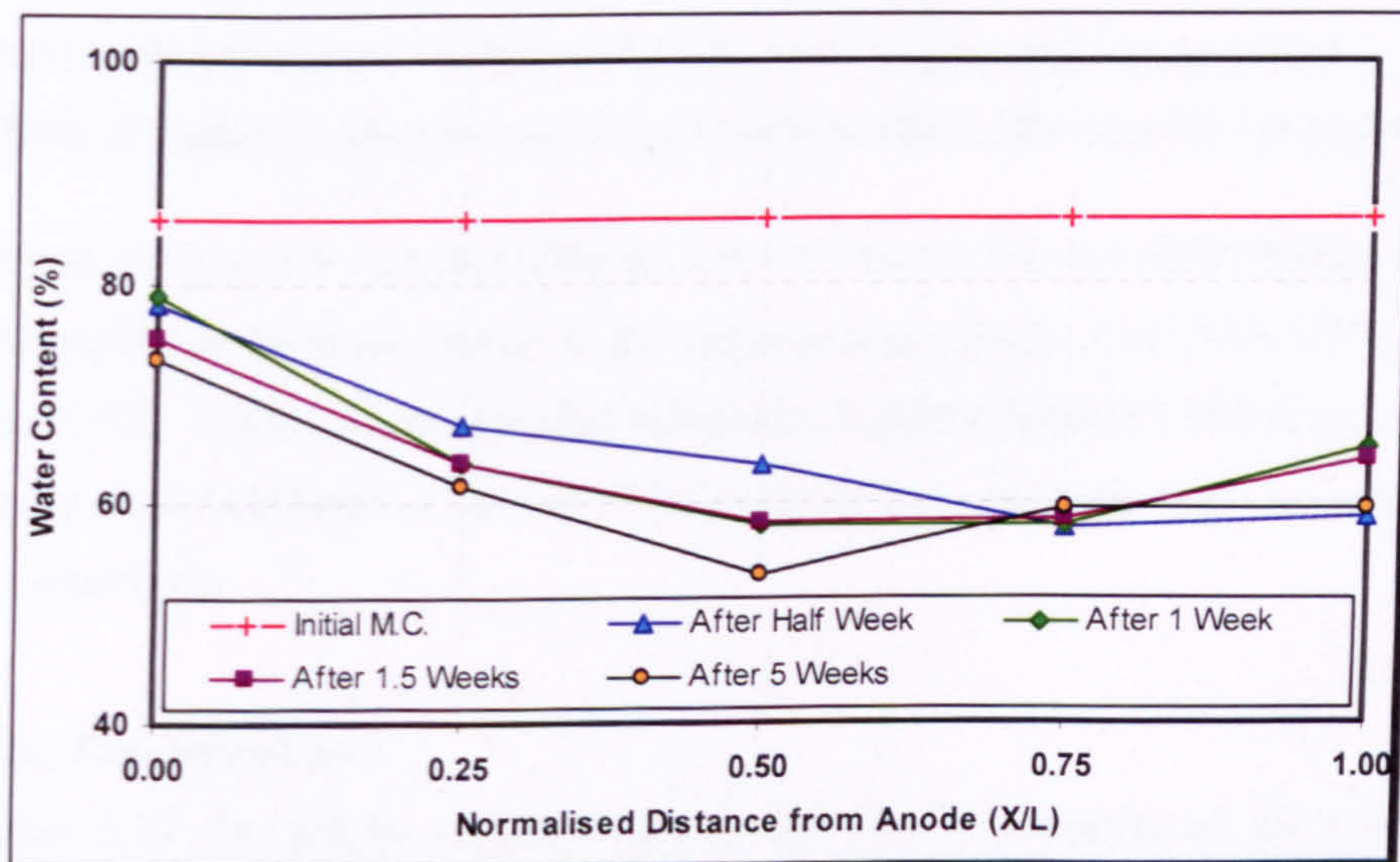


Fig 5.25 Variation of Average WC along Cell - with Intermittent Current

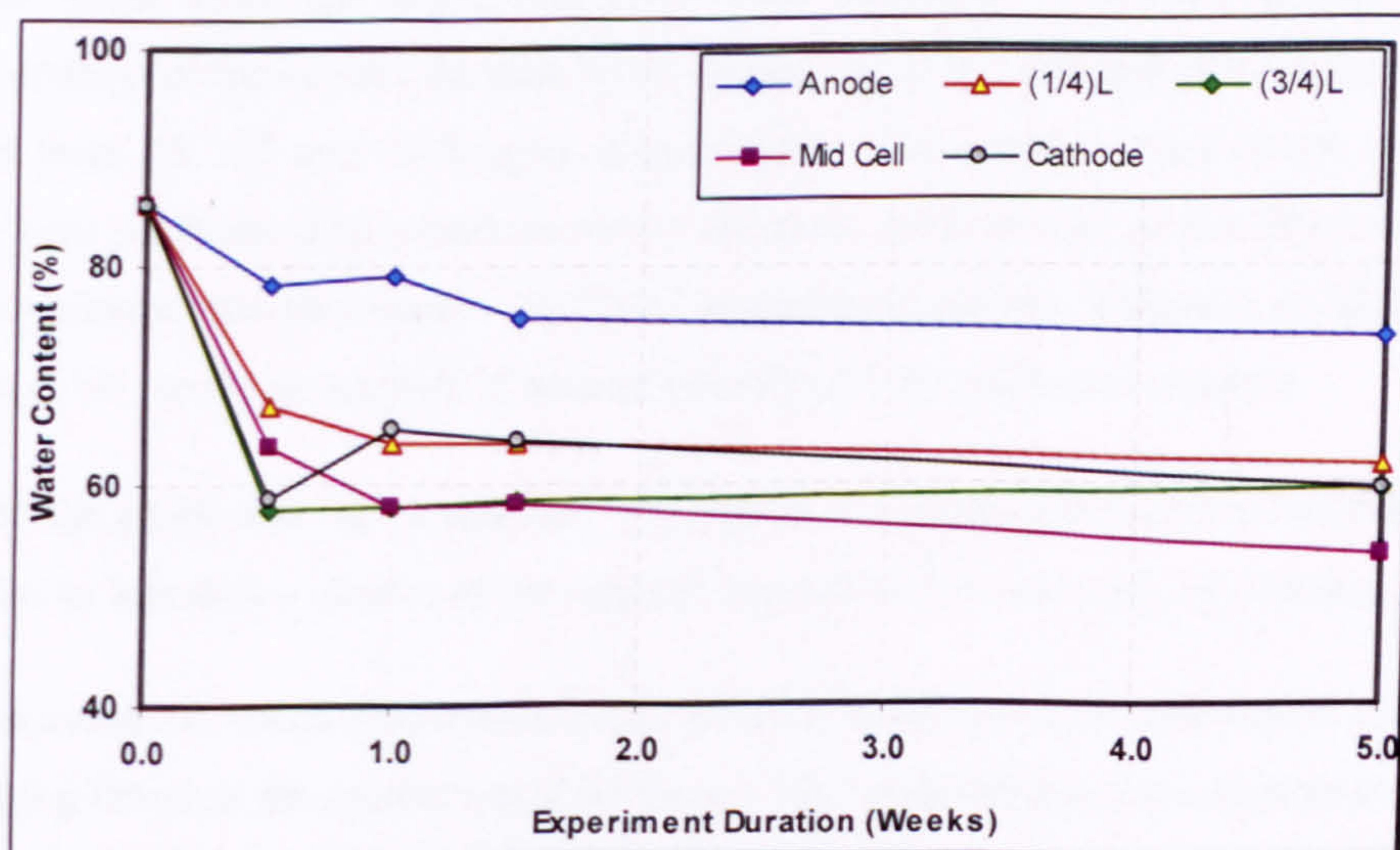


Fig 5.26 Variation of Average WC with Time - with Intermittent Current

Throughout testing, the uppermost average water contents were measured at the anode while the least were initially obtained at $\frac{3}{4}L$ before being recorded at the mid cell from one and half weeks onwards. It was also noted that the WC at $\frac{3}{4}L$ remained almost unchanged at 58.5% up to the fifth week. The decrease between one and half weeks and the fifth week for the anode and $\frac{1}{4}L$ was only 2% while that decrease over the same period at mid cell and cathode was 5%.

Also, further comparison shows that at any particular period, the WCs along the test specimen with intermittent current conditions were higher (difference within 1 to 10%) than those of respective positions of samples treated with continuous DC (in Figure 5.13).

By the end of the actual current-treatment time of 5 weeks, the recorded average values at the five positions from the anode to the cathode respectively were 73%, 62%, 53.5%, 59.5%, 59.5%. These values were also marginally higher (within 4% difference) than the respective results obtained at the end of the experiments conducted with constant current supply conditions.

(c) Zinc Concentrations

In Figure 5.27 the graphs of the temporal and spatial variation of the metal ions concentrations in 5 weeks of actual electrokinetic and soil flushing processes is presented.

Top of the Cells (Figure 5.27(a) and (d))

Results show from the start, that there were continual reductions in metal cation concentration at the anode, $\frac{1}{4}L$ and $\frac{1}{2}L$ until the end of the one and half weeks when the values were 13, 5.5 and 13.5mg/kg respectively. The contamination levels at each of these three positions then remained nearly the same until the end of the fifth week when the experiment was terminated. Identical responses were also reported, at all positions except at $\frac{1}{2}L$, in the anode half of specimens treated with continuous current.

At both the anode and $\frac{1}{4}L$, under both continuous and intermittent current test conditions, Zn^{2+} fell to less than a quarter of the original amount within one week of treating.

In contrast, at $\frac{3}{4}L$ metal ions concentration initially increased with time before peaking at 139mg/kg between the second and third week. This peak produced the highest amount of contamination concentration anywhere in the cells during clean up. Under the continuous

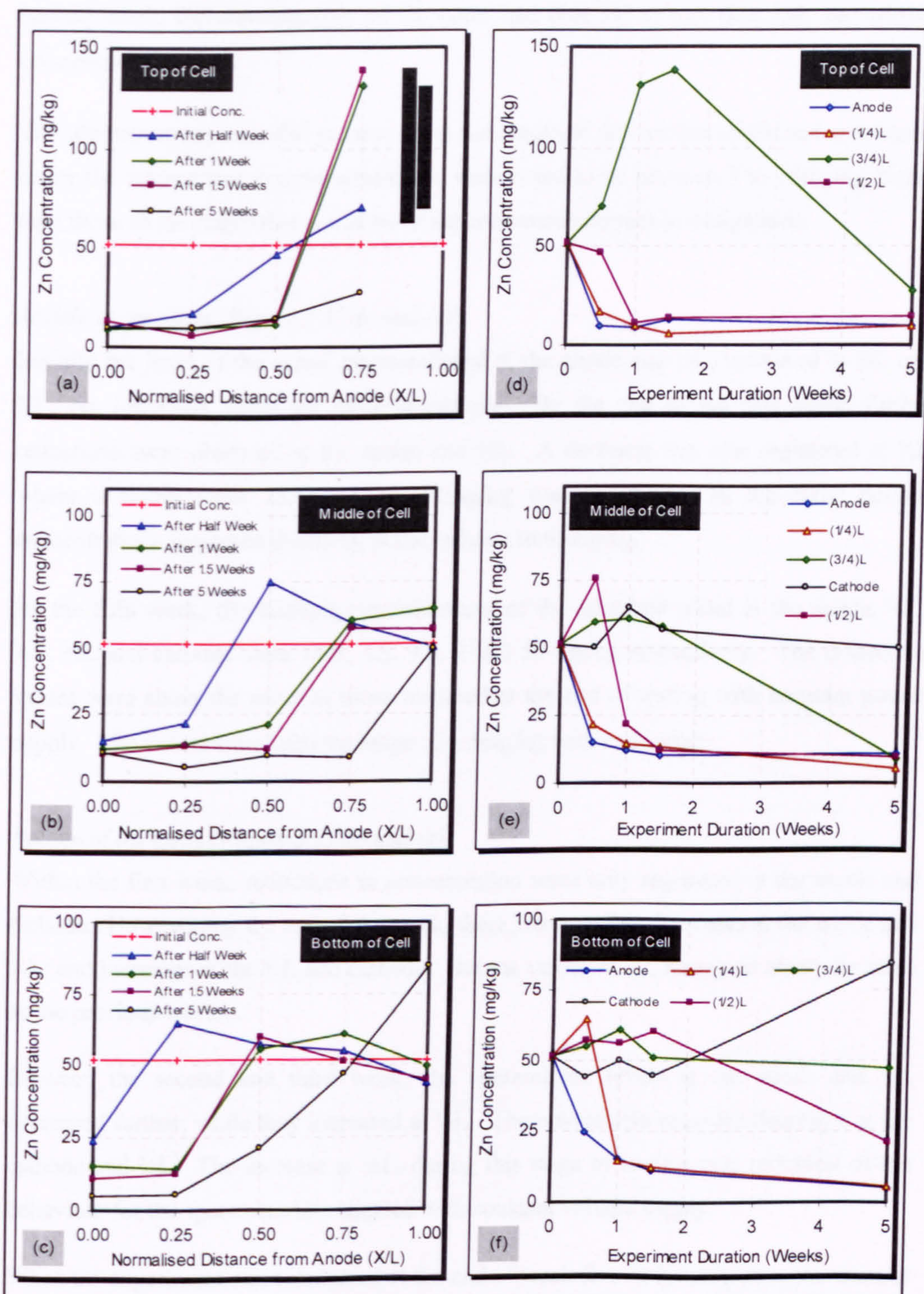


Fig 5.27 Variation of Zinc Concentration (a, b, c) along cell and (d, e, f) with Time - with Intermittent Current

DC, the concentration increased in the first week as well to nearly 65mg/kg. But from the second week, the concentration of the latter had reduced to less than half the original concentration.

The ultimate metal ions still present along the length of this section of the test specimen - under the intermittent current conditions, were noted to be between 3 to 14mg/kg higher than those of the respective positions of the continuous current investigations.

Middle of the Cells (Figure 5.27(b) and (e))

Initially the level of the metal cation reduced at the anode and $\frac{1}{4}L$, increased at $\frac{1}{2}L$ and $\frac{3}{4}L$, but remained about the same at cathode. By the end of the first week, further reductions were observed at the anode and $\frac{1}{4}L$. A decrease was also registered at $\frac{1}{2}L$ where a slump from 75.5mg/kg to 21mg/kg was observed. In the same period, concentrations increased distinctly at the cathode to 65mg/kg.

By the fifth week, the ultimate concentrations of the adsorbed metal at the anode, $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$ and cathode were 10.5, 5.5, 9.5, 9 and 50 mg/kg respectively. The respective values were about the same as those obtained at the end of testing with constant power supply. The values were with the range of ± 5 mg/kg with each other.

Bottom of the Cells (Figure 5.27(b) and (e))

Within the first week, reductions in concentration were only registered at the anode and cathode. However, by the end of the week, there were notable decreases at the anode and $\frac{1}{4}L$; and increases at the $\frac{3}{4}L$ and cathode. But the values at $\frac{1}{2}L$ remained about the same as the previous week's.

Between the second and third week, the contaminant levels at the anode and $\frac{1}{4}L$ decreased further, while they increased at $\frac{1}{2}L$. There were also recorded decreases at the cathode and $\frac{3}{4}L$. The increase at $\frac{1}{2}L$, during this stage of testing, was untypical of the behaviour for the specimens investigated with constant voltage supply.

When the experiment was terminated at the end of week five of investigation, the amount of the Zn^{2+} at the anode and $\frac{1}{4}L$ was virtually the same as that observed in the constant current investigations. However, the metal levels at the cathode end of the former

investigations were higher than those of the corresponding positions of the latter by between 13 and 43.5mg/kg.

Average Values

In Figure 5.28, the variation of the average Zn^{2+} concentrations along the specimens lengths is presented, while Figure 5.29 shows the variation of the cation concentration with time. Based on the average metal contamination values, it is evident that treatment with intermittent current caused:

- 1) an initial increase in metal cation levels in the middle vertical third of the cell, while the specimen extreme ends i.e. anode and cathode positions experienced falling heavy metal concentration values . This is clearly shown by the concentration plots along the cell (Figure 5.28). This initial behaviour was unique to only experiments conducted with intermittent currents. However, as the experiment duration increased, the concentration gradient increased in either direction towards $\frac{3}{4}L$ so that by the second and third weeks, this region was the most polluted.
- 2) a continuous fall in Zn amounts at the anode side of the cell (i.e. anode to $\frac{1}{4}L$) during the entire five weeks of electrokinetics and soil flushing processes (Figure 5.27). It is clear that only at these two positions were the positive cleaning results achieved continuously from start to finish.
- 3) a peak to be experienced at $\frac{3}{4}L$ peaking in the second week at 84mg/kg. Afterwards, there was a marked slump between the second and the fifth week.
- 4) increases at the cathode especially between one and half weeks and fifth week. By the termination of the experiments, the metal concentration was still increasing at the cathode. This was not the case in the continuous current situation. In that case, residual value concentration had been reached by the end of testing.

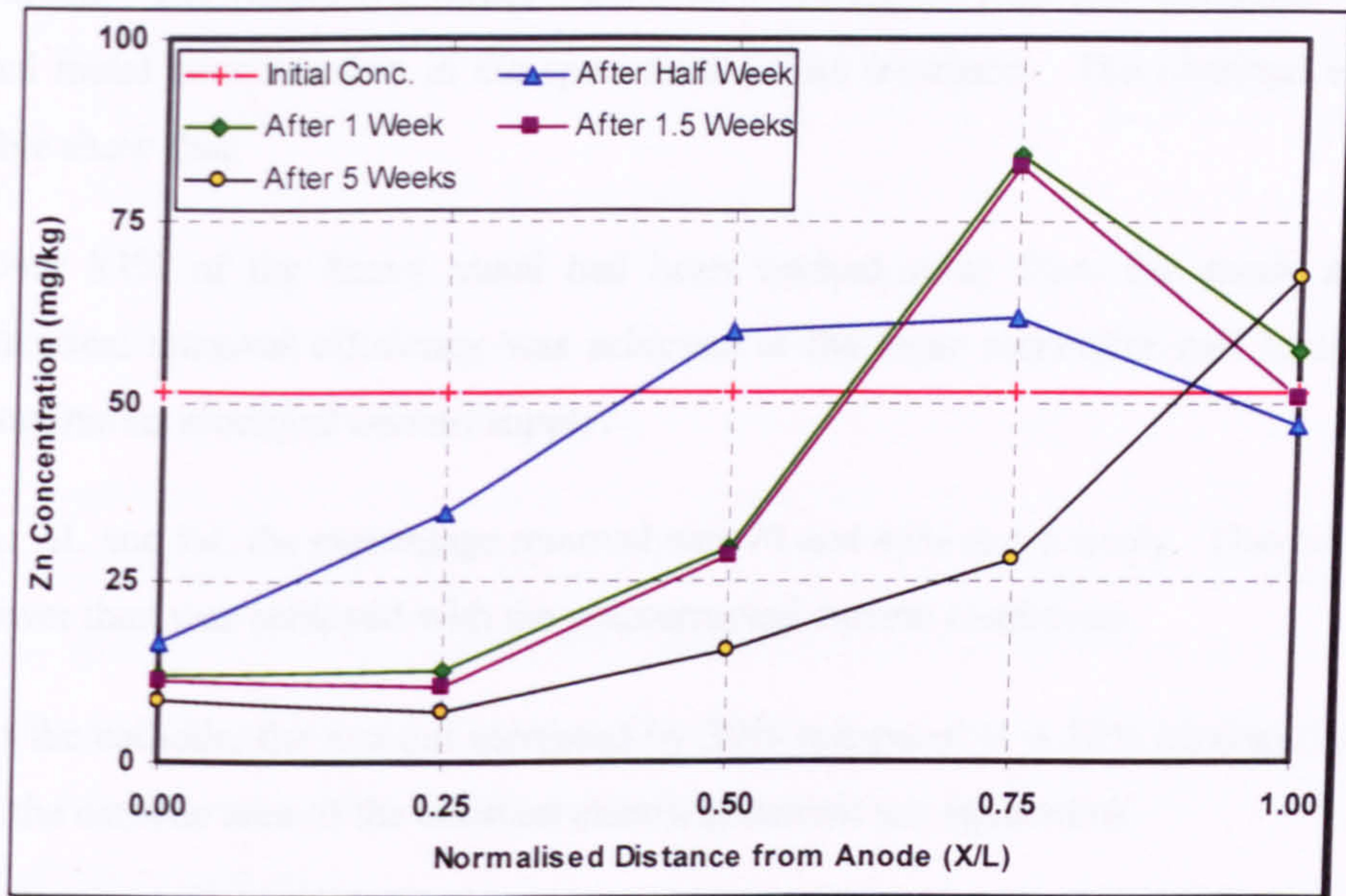


Fig 5.28 Variation of Average Zinc Concentration along Cell - with Intermittent Current

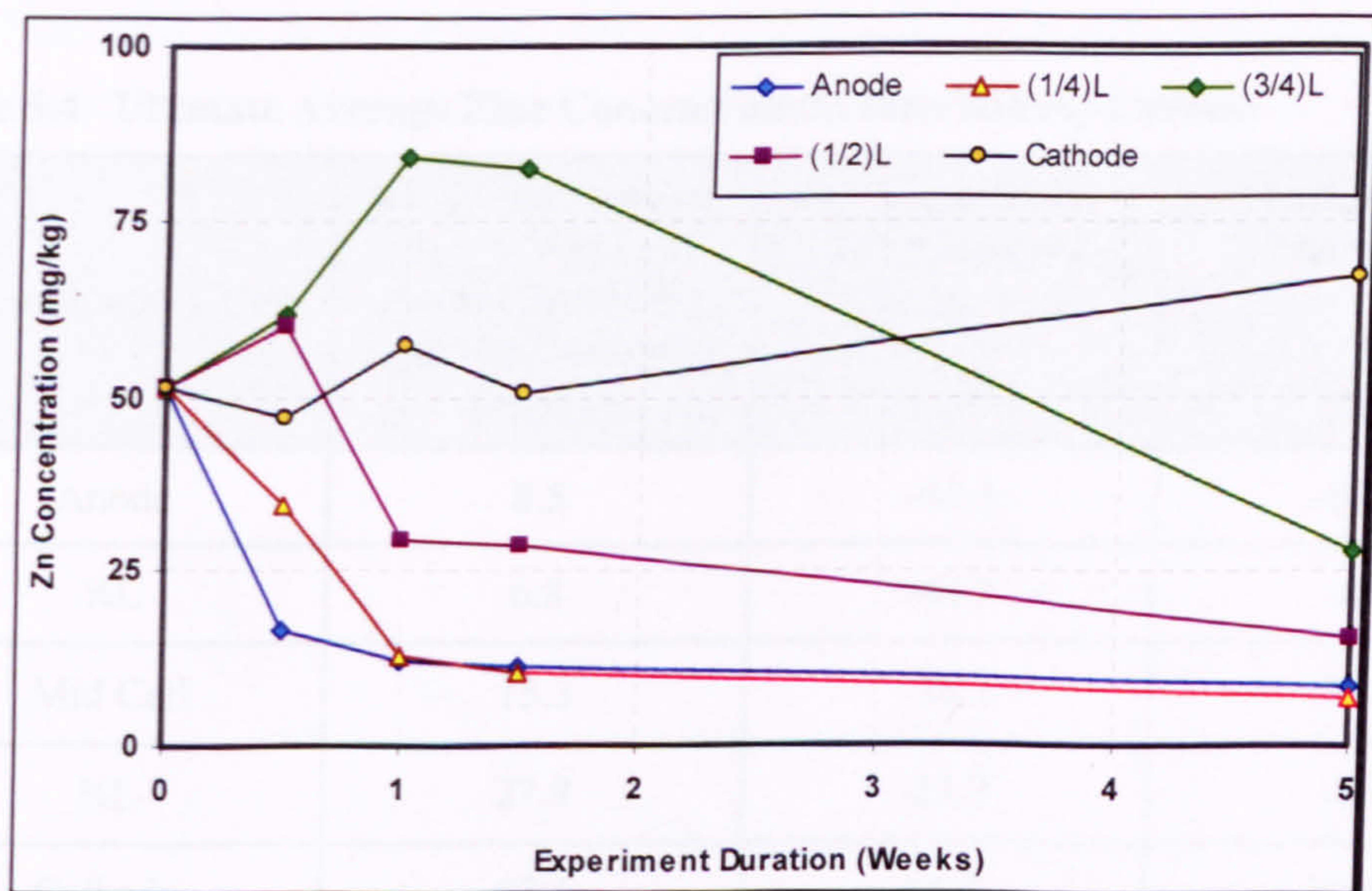


Fig 5.29 Variation of Average Zinc Concentration with Time - with Intermittent Current

Table 5.4 below shows the average Zn^{2+} still present in the soil specimen at the end of the experiment. The respective values were read from Figure 5.29 and compared with the original metal concentration in the specimens before treatment. The obtained values in the table show that:

- a) Over 83% of the heavy metal had been washed away from the anode and $\frac{1}{4}L$. Identical removal efficiency was achieved at the same respective cell section with continuous electrical current supply.
- b) At $\frac{1}{2}L$ and $\frac{3}{4}L$ the percentage removal was 70 and 46% respectively. This was much lower than was achieved with the uninterrupted current conditions.
- c) At the cathode, the amount increased by 30% compared to a 20% increase recorded at the cathode area of the constant electrical current test specimens.
- d) Because of intermittent current, there was less removal of the metal contaminant (from $\frac{1}{2}L$ to the cathode) as compared to the specimen whose current was run continuously.

Table 5.4 Ultimate Average Zinc Concentration: Intermittent Current

Position along Cell	Zn Concentration after 5 Weeks of Actual Switching on the Current (mg/kg)	Concentration Increase (+) / Decrease (-) (mg/kg)	Percentage Changes (+/-) (%)
Anode	8.5	-43.1	-83.5
$\frac{1}{4}L$	6.8	-44.7	-87
Mid Cell	15.2	-36.3	-70.5
$\frac{3}{4}L$	27.9	-23.7	-46
Cathode	67.3	15.8	30.5

5.2.4 Changing Water in Drainage Channels

Under this investigation, three 25mm thick drainage channels were aligned along the experiment soil sample length - at the quarter ($\frac{1}{4}$), mid cell ($\frac{1}{2}$) and three quarter ($\frac{3}{4}$) distances from the anode electrode - consequently subdividing the soil mass into four equal soil portions approximately 90 mm long (Figure 4.11). Deionised water was poured to each installed drainage channel to the height of the soil sample (150mm). Once the treatment process was started, by applying a constant voltage gradient of 0.5 V/cm across the test specimen, the channel waters were replenished with fresh deionised water every after 24 hours (Section 4.2.2.5). By periodically replacing the contaminated water in the channels with the 'clean water' - thereby increasing the soil surface area in contact with uncontaminated water during the electrokinetic process - it was anticipated this would improve the removal of the metals from the test soil mass. This section presents the results of this investigation.

(a) Electrical Current

Results of the temporal electrical current passing through the five test cells for the five week treatment period are shown in Figure 5.30 below. As in the previous investigations (Sections 5.2.1 to 5.2.3), results show a similar decline in electrical current with experiment duration. The prime fall in current values also occurred in the first week of treatment.

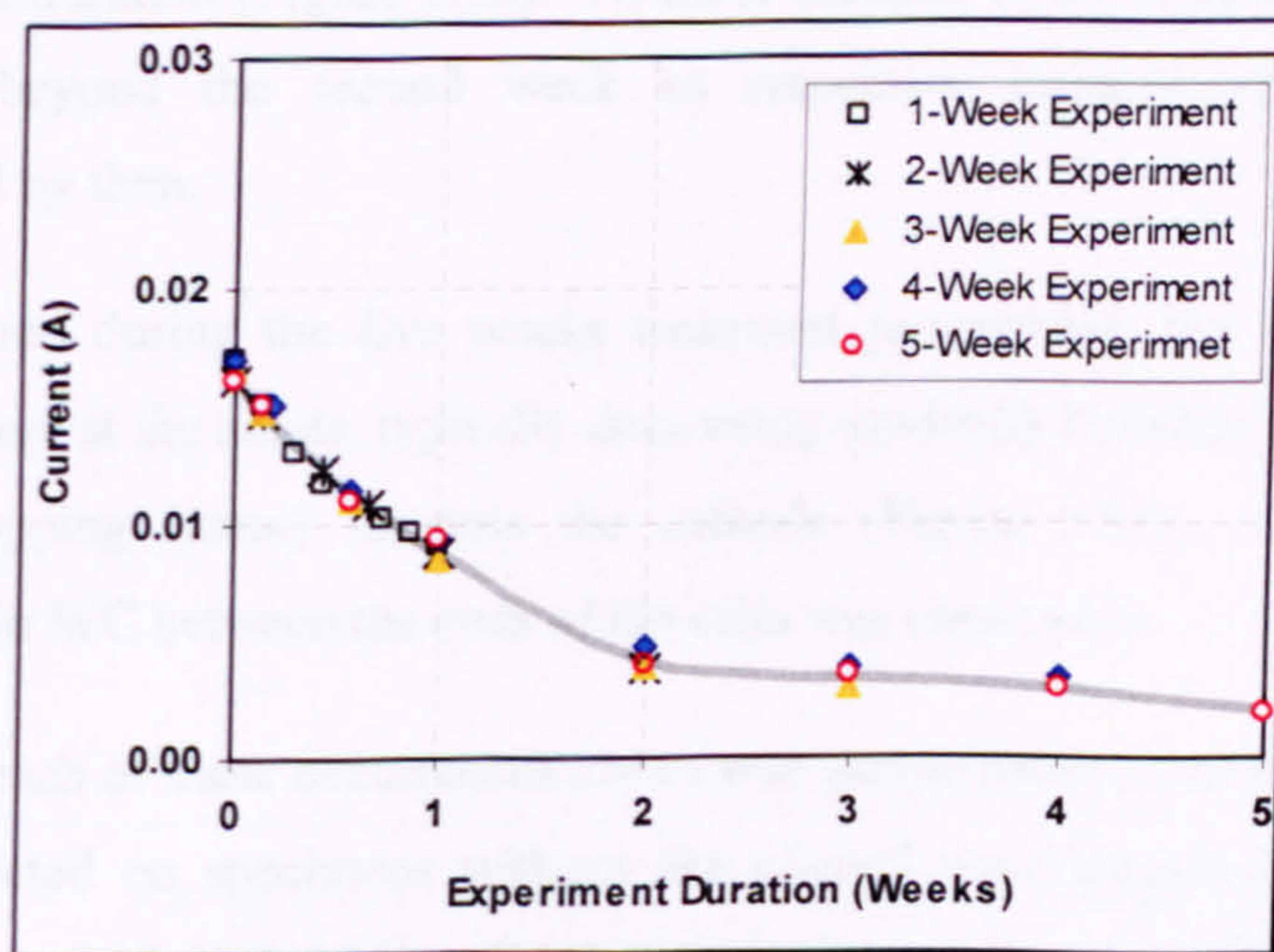


Fig 5.30 Variation of Current with Time with Flushing at Anode - with Replenished Drainage Channels

It is evident from the results that at any period during treatment, the measured current in this investigation was much lower than that of same sized specimens treated without replenished channels aligned in the soil mass (Section 5.2.1). For instance, the average initial current into the test cells of the former was measured as 0.0165A compared to 0.048A of the later. This was smaller by nearly 65%. Addition of deionised water-logged-drainage channels, therefore, appears to have had a reducing effect on the cell electrical current flow. The reasons for this and further explanations are given in Chapter 6.

Further observation of the results also showed that, though the initial current values obtained in this investigation were much lower than those obtained with the closed anode conditions, by the end of the first week onwards, the current of the closed anode had dropped lower than that of this investigation. The explanation for this occurrence, again, is presented in Chapter 6.

(b) Water Content

The average results of the spatial and temporal WC of electrokinetic tests conducted on open anode specimens fitted with waterlogged chambers aligned along the soil mass, computed from Figure A5.2 in the appendix, are given in Figures 5.31 and 5.32. It is demonstrated from the results that:

- 1) the WC at all the sampled positions of the cells generally decreased with increase in experiment duration (Figure 5.32). At most sections of the cell, the decreases were marginal beyond the second week as respective residual values were being established by then.
- 2) at any period during the five weeks treatment programme, the highest cell water contents were at the anode, typically decreasing gradually between the anode and $\frac{3}{4}L$ before dropping steeply towards the cathode (Figure 5.31). At any time, the difference in WC between the ends of the cells was about 15%.

It is noted that each of these occurrences above was synonymous to what was observed in the tests conducted on specimens without the aligned waterlogged drainage channels (refer to Figures 5.12 and 5.13). Further comparison, shows that at any period in reference, higher WC values were obtained in cells treated with waterlogged drainage

channels. This therefore implied that additional of these water-filled channels increased the soil area in contact with water during the electrokinetic process consequently increasing the cell water contents.

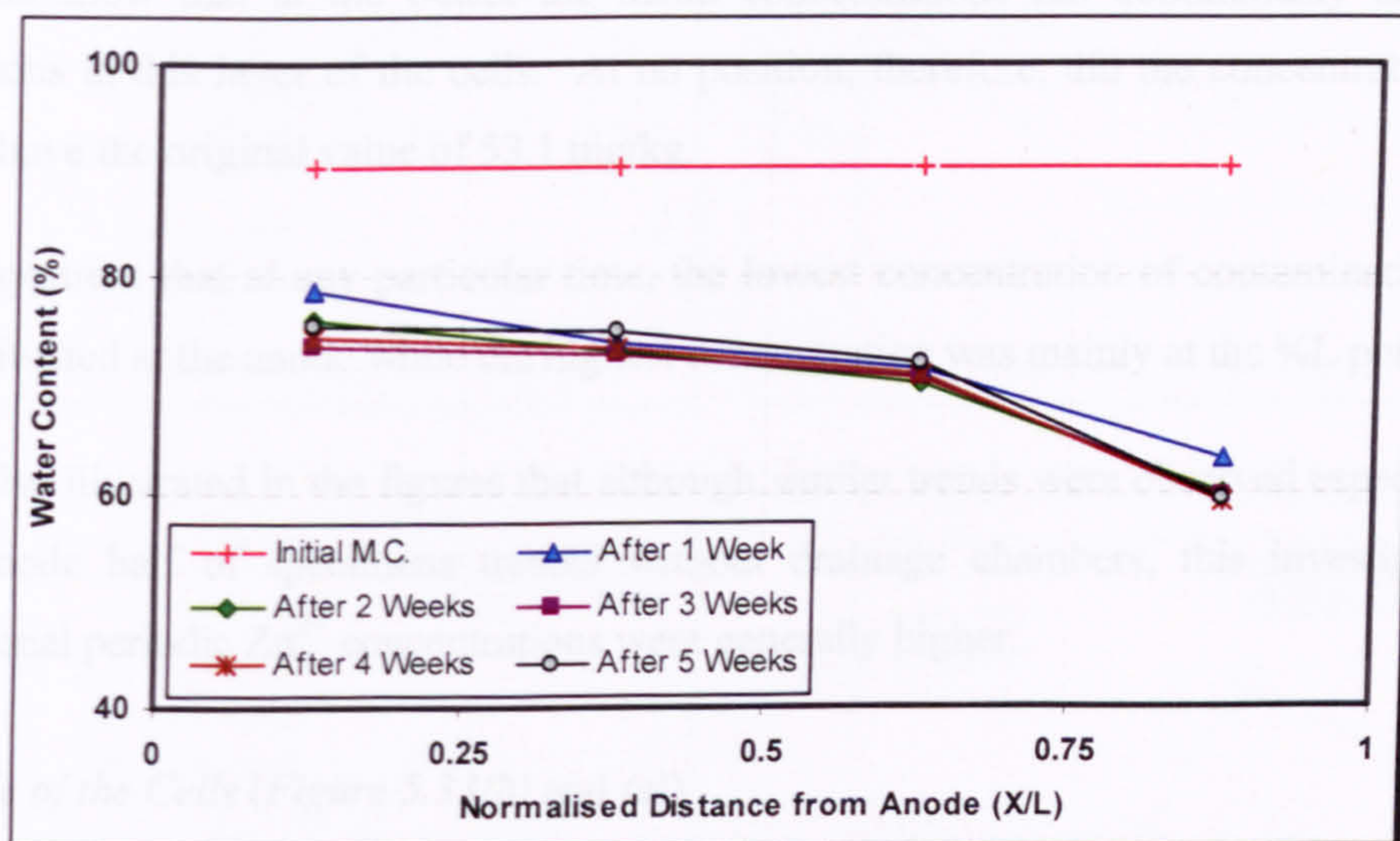


Fig 5.30 Variation of Average WC along Cell – with Replenished Drainage Channels

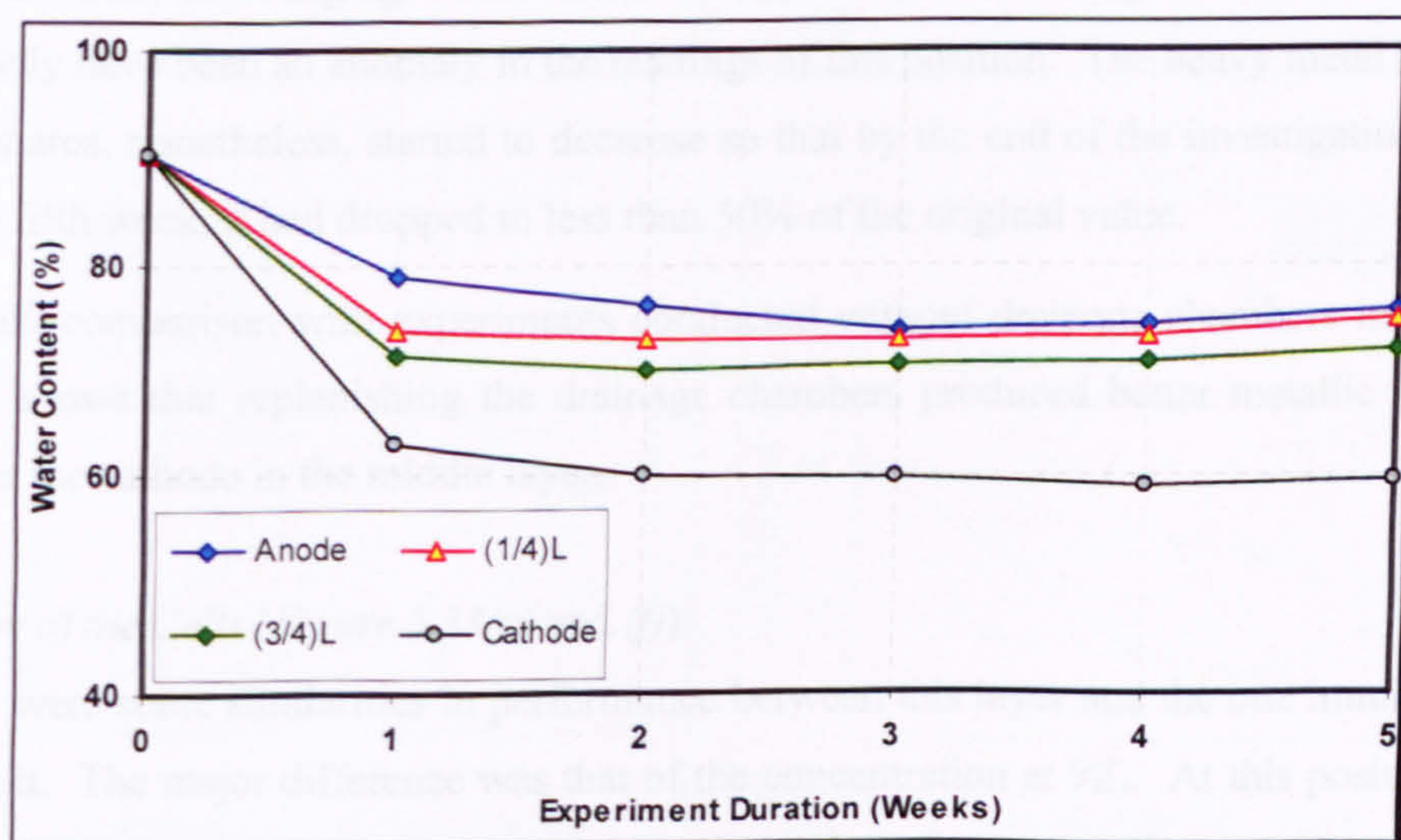


Fig 5.32 Variation of Average WC with Time – with Replenished Drainage Channels

(c) Zinc Concentrations

The temporal and spatial changes in the concentration of the Zn^{2+} are presented in Figure 5.33.

Top of the Cells (Figure 5.33(a) and (d))

Results show that at the outset the metal concentrations fell continuously at all the positions in this layer of the cells. At no position, therefore, did the concentration ever rise above the original value of 53.1 mg/kg.

It is apparent that at any particular time, the lowest concentration of contaminating ions was situated at the anode while the highest concentration was mainly at the $\frac{3}{4}L$ point.

It is also illustrated in the figures that although similar trends were observed especially in the anode half of specimens treated without drainage chambers, this investigation's positional periodic Zn^{2+} concentrations were generally higher.

Middle of the Cells (Figure 5.33(b) and (e))

The behaviour in this layer was quite different to that of the layer above. Over the initial two weeks there was a continual drop in Zn metal cations along the entire length of the cell. However, in the third week, there was a distinct rise near $\frac{3}{4}L$ from 34mg/kg (in the second week) to 73mg/kg. This uncharacteristic rapid amassing of ions at $\frac{3}{4}L$ could probably have been an anomaly in the readings of this position. The heavy metal build-up at this area, nonetheless, started to decrease so that by the end of the investigation period in the fifth week, it had dropped to less than 50% of the original value.

Overall, comparison with experiments conducted without drainage chambers in the soil mass, shows that replenishing the drainage chambers produced better metallic removal only at the cathode in the middle layer.

Bottom of the Cells (Figure 5.33(c) and (f))

There were some similarities in performance between this layer and the one immediately above it. The major difference was that of the concentration at $\frac{3}{4}L$. At this position, the contaminating cation initially decreased like in all the other areas. However, in this case, it started rising in the second week continuing to the third. The peak at the third week was

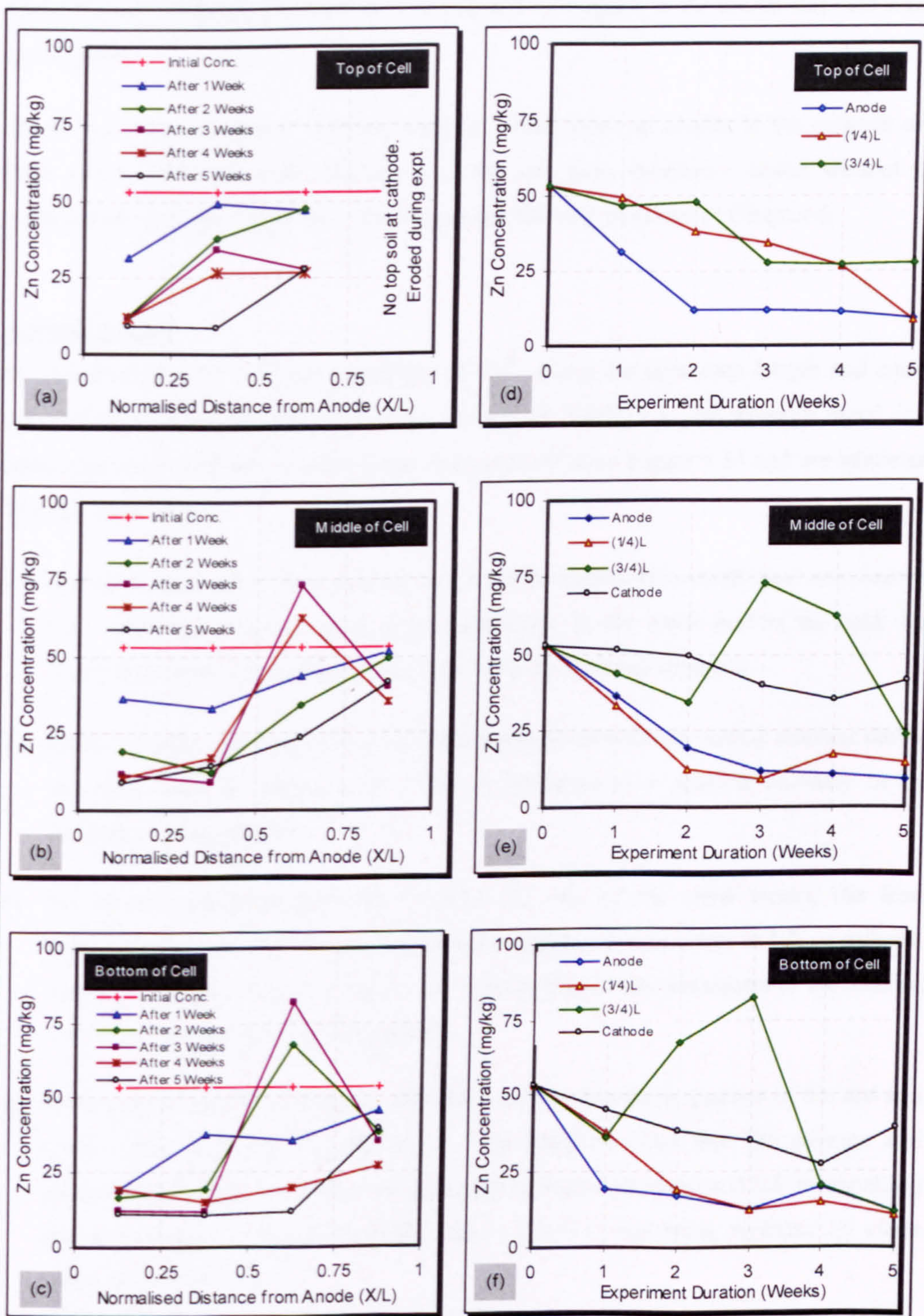


Fig 5.33 Variation of Zinc Concentration (a, b, c) along cell and (d, e, f) with Time - with Replenished Drainage Channels

82mg/kg. This was the highest anywhere in the specimen during the operation. There was a distinct slump in the value to 20mg/kg and 11.6mg/kg in the fourth and fifth weeks in that order.

Once more, this treatment method produced better clean-up results at the cathode area with lower metal removals elsewhere in the cell than specimens tested without the replenished drainage chambers. The reasons for this are presented in Chapter 6.

Average Values

In Figures 5.34 and 5.35, the variations of Zn^{2+} along the specimen length and cation concentration with time are presented. While in Table 5.5, the average metal ions remaining at the end of the experiment were read off from Figure 5.35 and are tabulated. The results confirm:

- 1) a general decrease in heavy metals ions with increase in time at all other areas except $\frac{3}{4}L$. However, the rate of reduction, especially in the anode half of the cells was lower than was observed with specimens with no drainage channels.
- 2) falling contaminating species at $\frac{3}{4}L$ interrupted by an uncharacteristic increase during the third week of experiments. This is attributed to a possible anomaly in the readings at this position.
- 3) for all concentration gradients (besides the one of the third week), the least concentration was at the anode whereas the uppermost was either at $\frac{3}{4}L$ or cathode. This is noticeably shown in Figure 5.35 and reaffirmed that the stream of the metallic ions was in the direction of the cathode.
- 4) lower percentage metal removal efficiency achieved in three quarters of the test soil mass (refer to Table 5.5 and 5.2). It is therefore clear that the average end performance results were not at all improved between the anode and $\frac{3}{4}L$ by installing the water-logged drainage channels whose solution was being replaced by clean water every 24 hours.
- 5) heavy metal clean up results tremendously improved at the cathode (refer to Table 5.7 and 5.4). The average Zn concentration reduced by 25% as compared to the

increases which were reported for both the 150mm and 300mm high samples tested without the drainage channels.

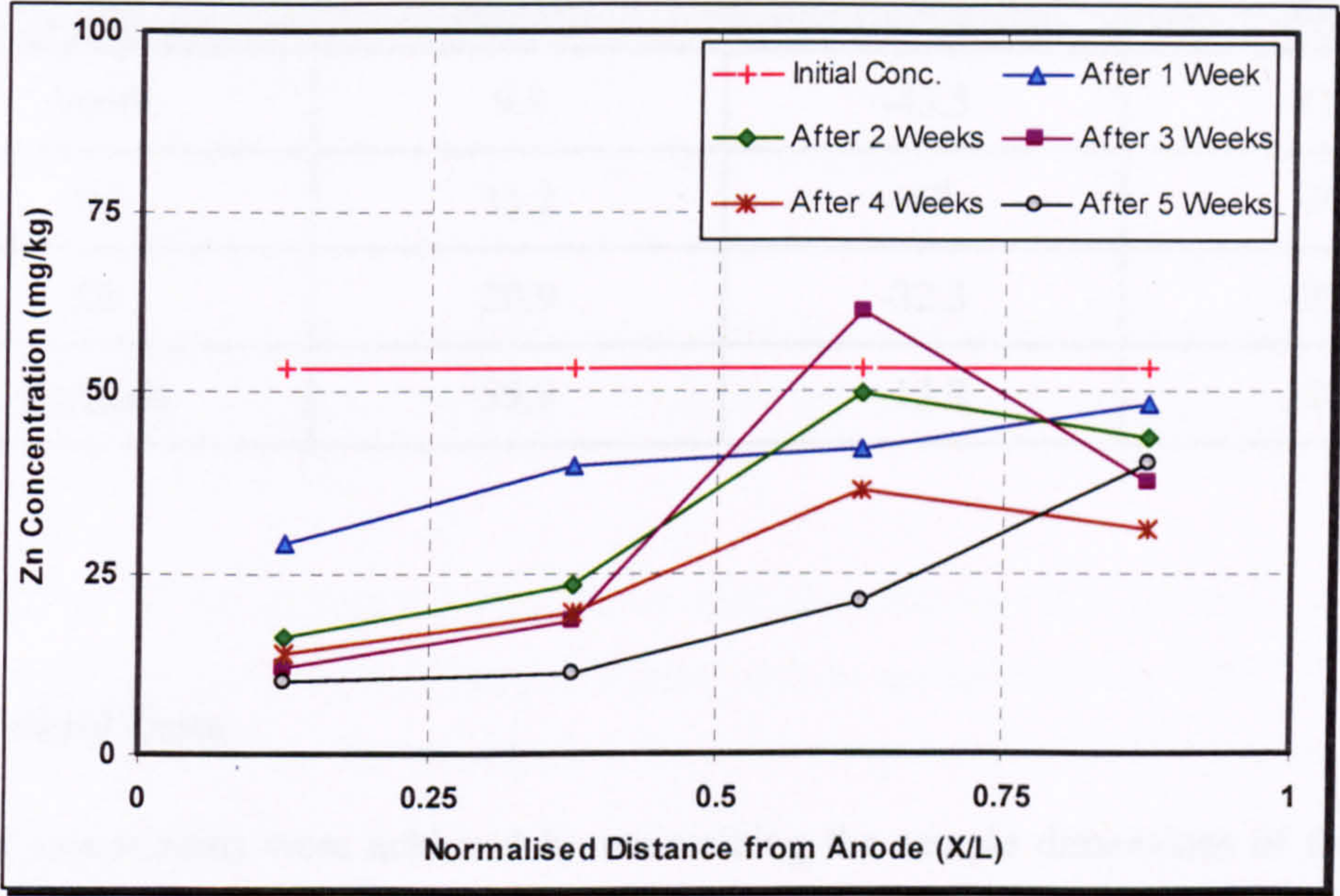


Fig 5.34 Variation of Average Zinc Concentration along Cell - with Replenished Drainage Channels

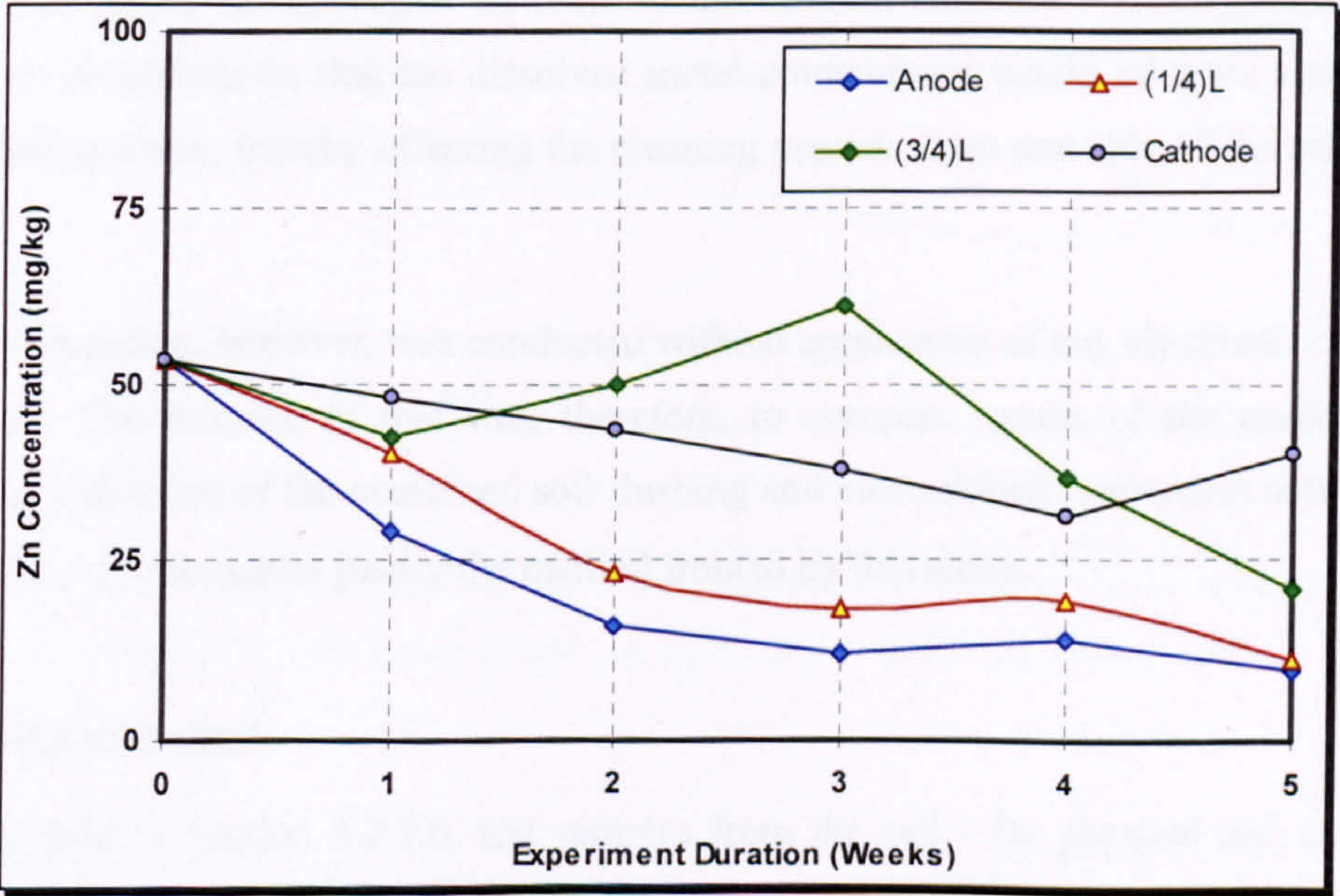


Fig 5.35 Variation of Average Zinc Concentration with Time - with Replenished Drainage Channels

Table 5.5 Average Zinc Concentration after 5 Weeks Had Elapsed: With Replenished Drainage Channels

Position along Cell	Zinc Concentration after 5 Weeks (mg/kg)	Concentration Increase (+) / Decrease (-) (mg/kg)	Percentage Changes (+/-) (%)
Anode	9.8	-43.3	-81.5
¼L	11.2	-42	-79
¾L	20.9	-32.3	-60.7
Cathode	39.9	-13.2	-25

5.3 Control Tests

Control experiments were achieved by maintaining the sample dimensions of the Two Process Approach (open anode) investigation (refer to Section 5.2.1). In addition, deionised water was also constantly supplied at one end of the test cell (flushing chamber side). Due to the hydraulic gradient between the test cell ends, water continuously permeated across the specimen en route to the effluent chamber. The hypothesis was based on consideration that the dissolved metal contaminant would advance along with the flushing water, thereby effecting the cleaning process from one side of the cell to the other.

The investigation, however, was conducted without application of any electrical current to the cell. The purpose of this was, therefore, to compare results of the unaided soil flushing with those of the combined soil flushing and electrokinetic processes obtained in Section 5.2.1 – thereafter justify the method fronted by this study.

(a) Water Content

As discussed in Section 4.2.2.6, test samples from the cell - for physical and chemical analysis - were only retrieved at the beginning and end of the five weeks testing programme. Therefore Figure 5.36, below, shows only results of the initial and average

final WC distribution along the normalised horizontal length of the experiment soil specimens. The latter was determined from the results presented in Figure A5.3. It is noticeable from the graph in Figure 5.36 that after five weeks of water flushing:

- 1) the soil water content had reduced at all sections of the cell. By the time the experiment was ended, the WC amounts had reduced from the initial value of 85.7% to 80.5% and 74.5% at the Flushing chamber and Effluent chamber test cell sides respectively.
- 2) the highest WC was at the flushing chamber side and reduced along the cell in the direction of the Effluent chamber. At end of the test, the WC gradient between the two cell ends was 6%.

Comparison of the treatment results shows that, the ultimate WCs of the control test specimens were higher than of samples treated with an applied current. This is evidence that at any period during the investigation, the control experiments samples were wetter.

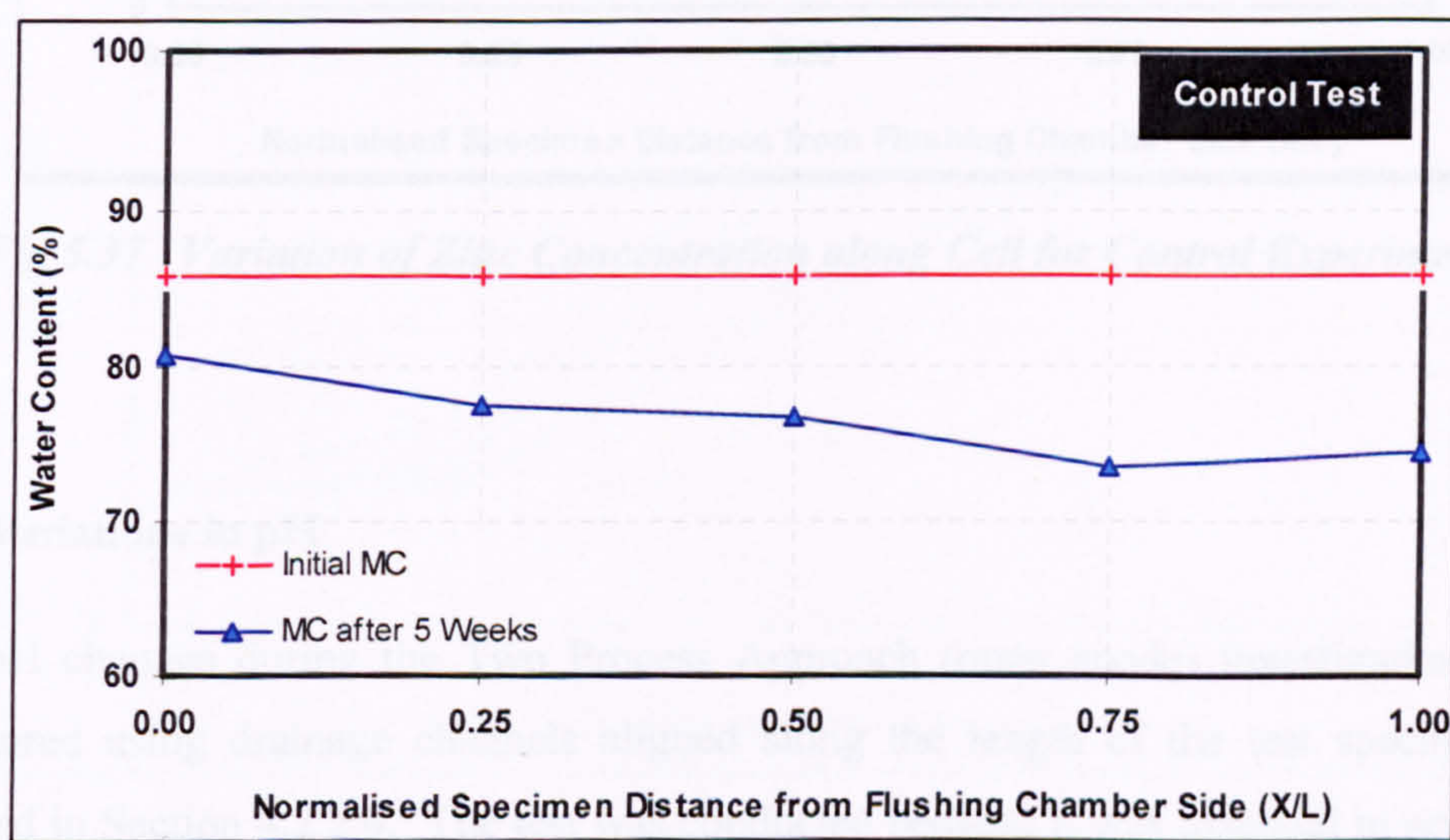


Fig 5.36 Variation of WC along Cell for Control Experiments

(b) Zinc Concentrations

Figure 5.37 shows the Zn^{2+} distribution along the test cell at the beginning and end of treatment. The results in the graph show very minor differences between the initial (49.04

mg/kg) and final metal concentrations in the test specimen. Slight increases in metal levels were observed in the sample at the Flushing chamber side and $\frac{3}{4}L$ position, and seemed to be balanced by small decreases at $\frac{1}{4}L$ and $\frac{1}{2}L$. The ultimate overall average concentration of the metal ions was 48.8mg/kg. This implies that after the five weeks of water flushing, the contaminant concentration had reduced by only a meagre 0.14mg/kg which yields a 0.3% metal removal. Based on Zn^{2+} removal, water flushing alone produced the worst cleaning results of the all the investigations.

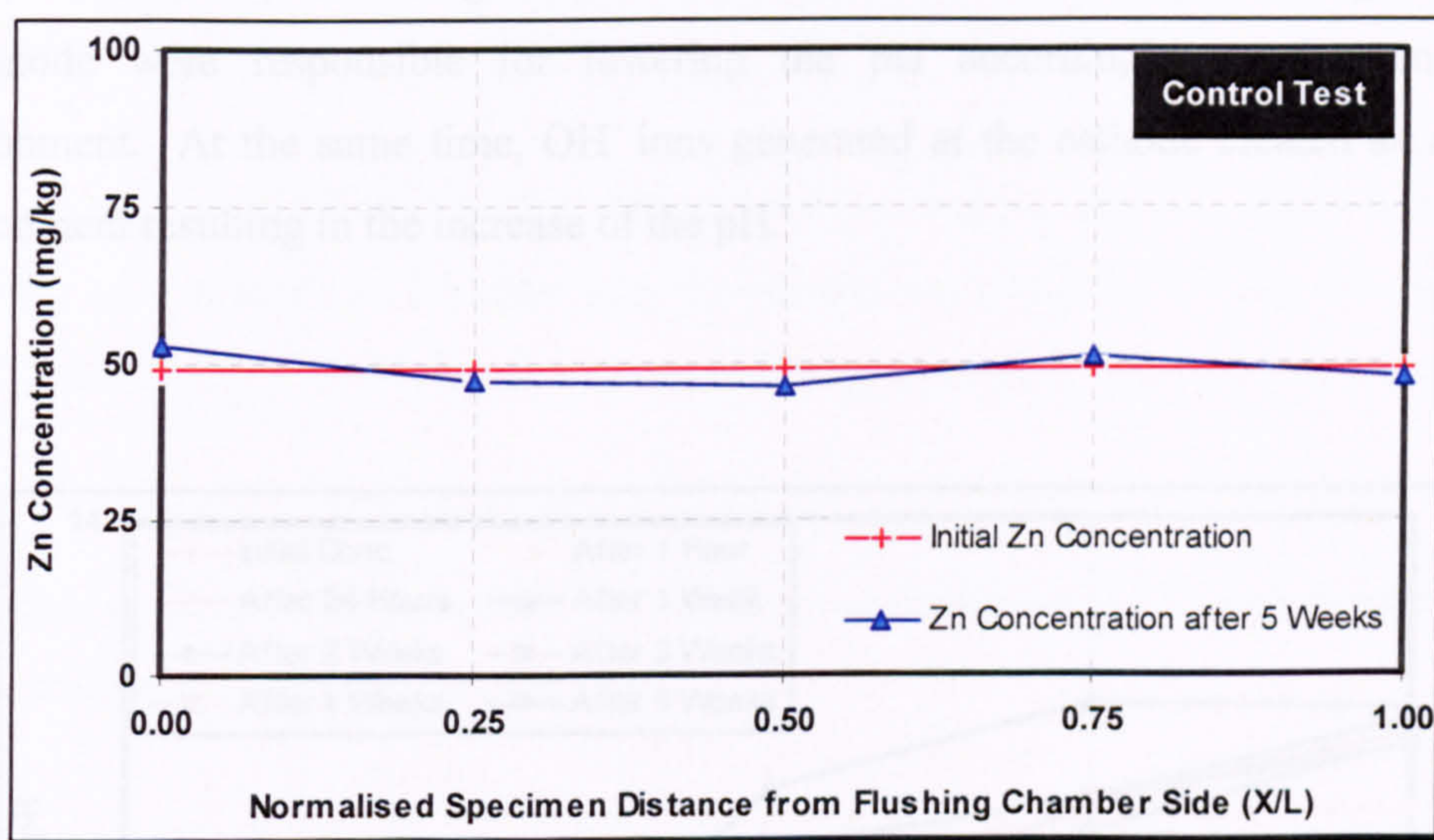


Fig 5.37 Variation of Zinc Concentration along Cell for Control Experiments

5.4 Variations in pH

The pH changes during the Two Process Approach (open anode) investigations were monitored using drainage channels aligned along the length of the test specimens as detailed in Section 4.2.2.4. The test was conducted because it was essential to scrutinize the changes in the pH of the electrolyte in the soil due to five weeks of collective effect of electrokinetic and soil flushing processes. The spatial and temporal pH changes in the electrolyte trapped in the channels are displayed in Figures 5.38 and 5.39. As already explained in Section 4.2.2.4, the pH for the One Process Approach could not be investigated using the drainage channel method.

The test results demonstrate that the pH increased marginally at $\frac{1}{4}L$, $\frac{1}{2}L$, $\frac{3}{4}L$, and cathode positions initially but remained similar to the original value of 5.4 at the anode. Nonetheless, all the obtained values along the cell remained acidic. Towards the end of the first day (24 hours), the pH was already basic and still rising at $\frac{1}{2}L$, $\frac{3}{4}L$ and cathode. The uppermost values were observed at $\frac{3}{4}L$ and the cathode both at the same pH of 8.5. The pH at the anode and $\frac{1}{2}L$ was already acidic and had dropped to 2.3 and 3.3 respectively. Consequently the pH values were by then establishing extreme values at the electrodes. These values indicated that the electrolysis reactions, already discussed in Section 2.3.2.1, were occurring at the electrodes. In these reactions, H^+ ions generated at the anode were responsible for lowering the pH accordingly creating an acidic environment. At the same time, OH^- ions generated at the cathode created an alkaline environment resulting in the increase of the pH.

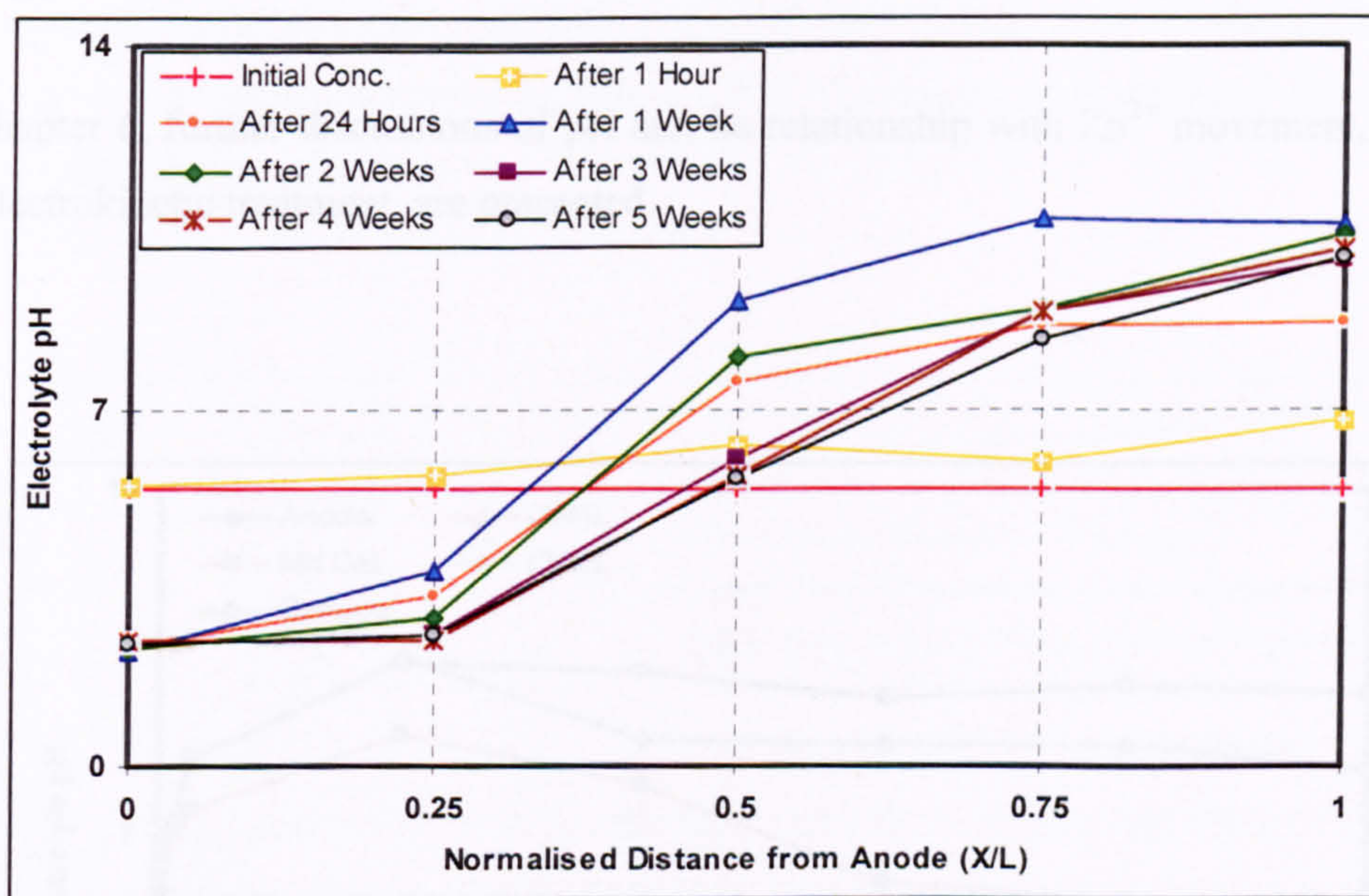


Fig 5.38 Variation of pH of Electrolyte along Cell – Using Drainage Chambers Method

By the end of the first week, the highest pH had been recorded at $\frac{3}{4}L$ and the cathode at 10.6 and 10.5 respectively. The pH values at $\frac{1}{4}L$ and $\frac{1}{2}L$, correspondingly at 3.8 and 9.1, were greater than the respective pH values just 24 hours after start of treatment. The general increase in pH along two thirds of the cell could indicate that the base front was

probably advancing towards the anode faster than the acid front. At that time, the pH at the anode remained unchanged at 2.3.

In the second and third weeks, a reduction in pH was noted at four positions out of five (all except at the anode itself). The most prominent decline was at the middle of the cell. The values at the anode side increased but only by fractions of pH points. The values at the end of the third week, from the anode in the direction to the cathode, were 2.4, 2.6, 6.0, 8.8 and 9.8 in that order. Distributions of pH across the soil at this stage of processing illustrated that the acid front developed at the anode was advancing towards the cathode faster than the base front.

In the fourth week there were further reductions at $\frac{1}{4}L$ and $\frac{1}{2}L$ and very slight increases at the anode and cathode. At the same time the pH was unchanged at $\frac{3}{4}L$. By the end of the investigation in the fifth week, the residual pH along the cell length was 2.4, 2.6, 5.6, 8.3, and 9.9.

In Chapter 6, further discussions of pH and its relationship with Zn^{2+} movement, during the electrokinetic treatment, are presented.

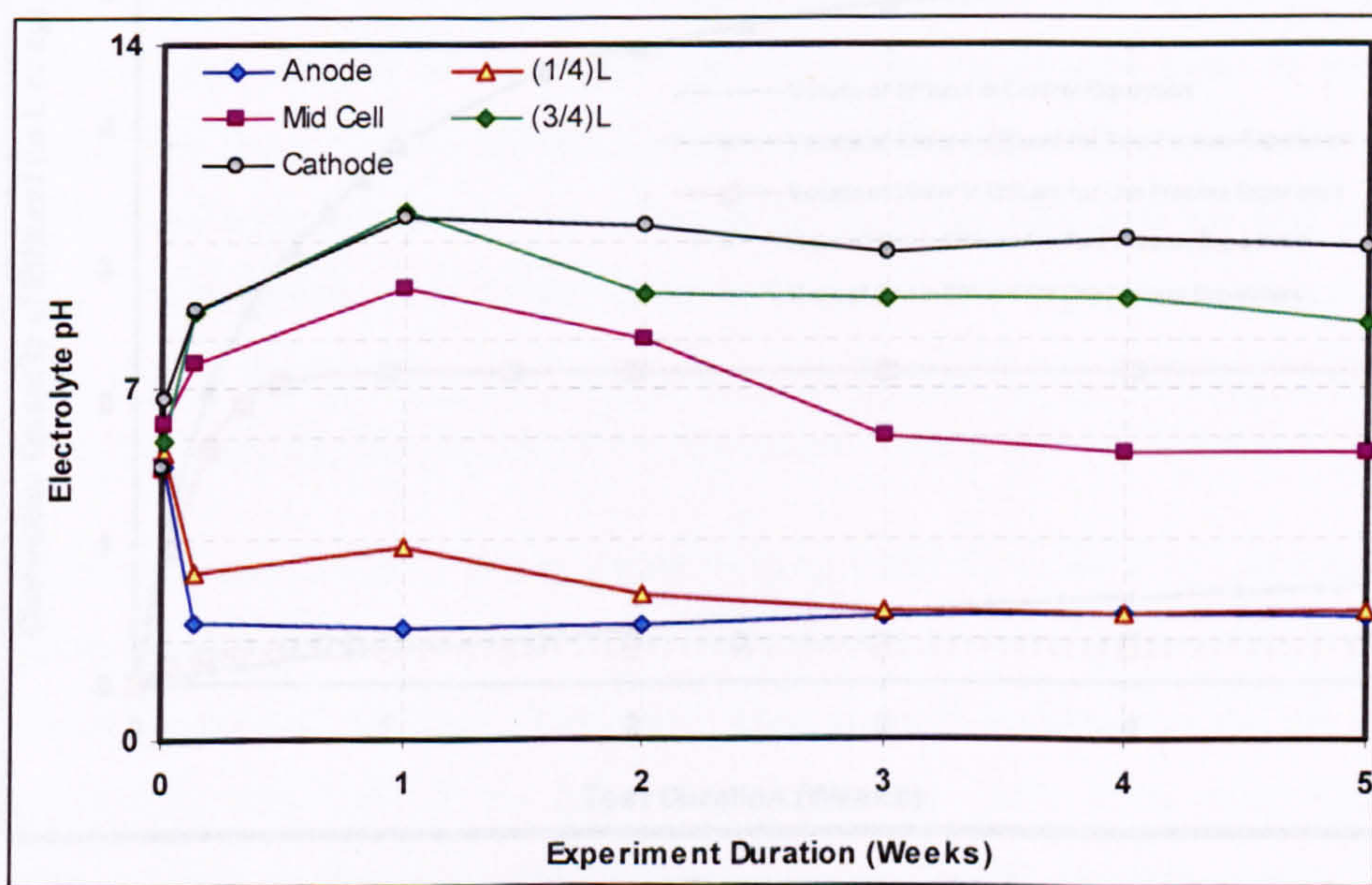


Fig 5.39 Variation of Electrolyte pH with Time – Using Drainage Chambers Method

5.5 Effluent

The volumes of the effluents separately collected during treatment of the test soil specimens, under the Control, the One Process and the Two Process Approach conditions, were periodically measured. The respective solution pH and concentrations of Zn^{2+} in the effluent water and suspended solids were determined. The metal contaminated solution discharges from the electrokinetic experiments (i.e. One and Two Process Approach tests) were a direct response of the applied DC voltage as well as water flushing for the latter treatment condition. While the effluent trickling from the control experiments, (treated by supplying deionised water on one vertical face of the soil specimen and letting it flow freely under the hydraulic gradient across the soil), was due to water seepage only. This section presents the results of the tests conducted on the respective effluents.

(a) Effluent Quantity

The relationship between the cumulative effluent flow volume and the elapsed time for the three investigations is shown in Figure 5.40. The values were obtained from Tables A5.3 to A5.5 in the appendix.

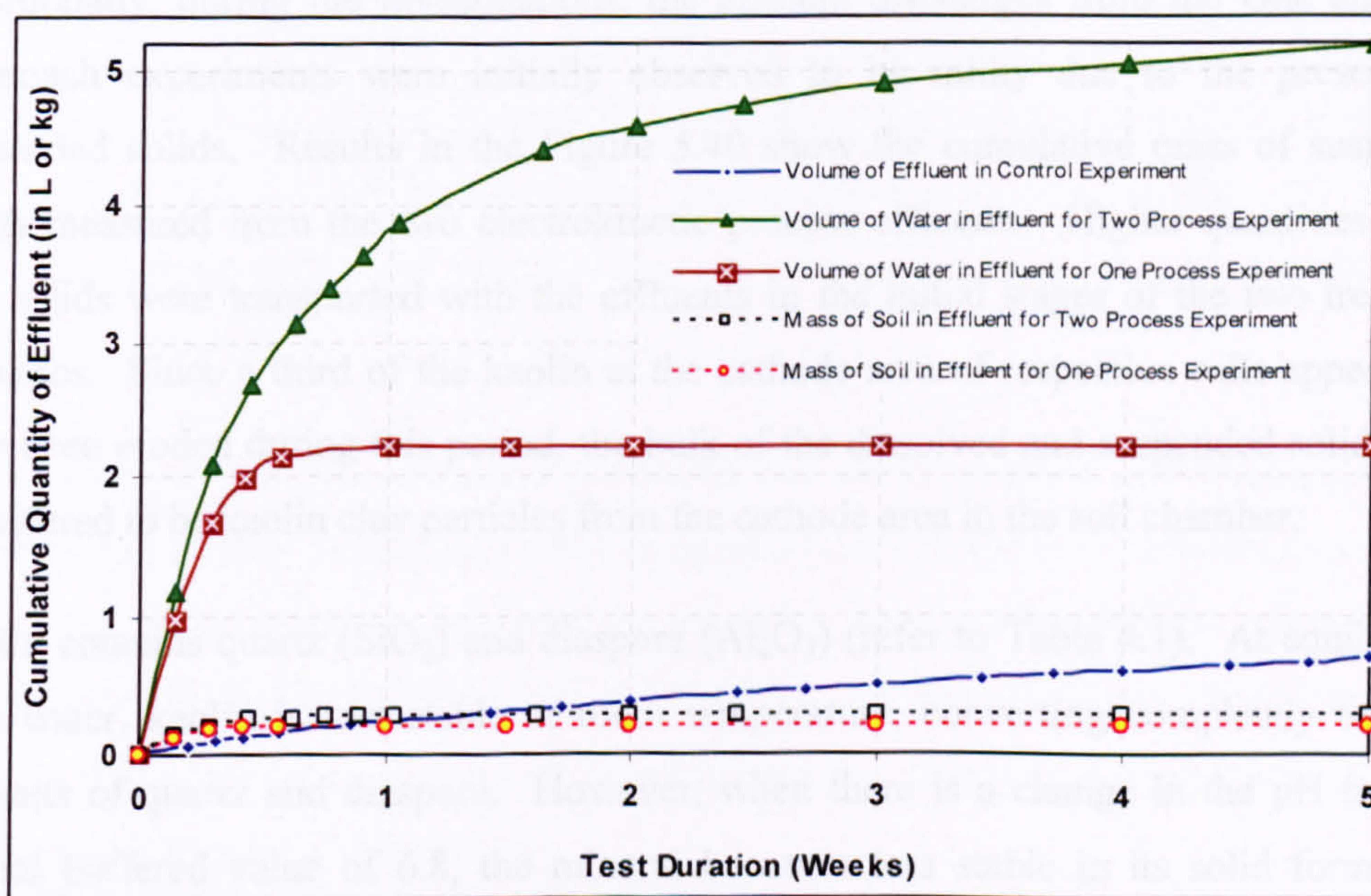


Fig 5.40 Temporal Variations of Effluent Flow Volume and Mass of Suspended Kaolin for the Different Treatment Processes

In Figure 5.40, the effluent discharges from the control experiments were in general at a constant rate while those from electrokinetic experiments decreased with time, with the highest amount of purge water measured in the first hours of the experiments. The latter situation indicated that the electroosmotic flow rate was highest in the initial stages when the measured current in the respective cells was observed to be highest (Figures 5.1 and 5.9).

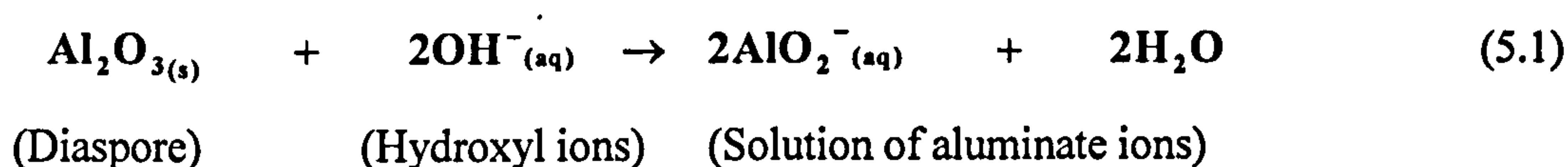
Over any period, the electrokinetic treatments clearly generated greater volumes of effluent water than the control experiments. The application of the electric field caused several effects in the test soil specimens but it is electroosmosis which was considered to be the dominant process for the mass movement of water from the electrokinetic cells.

By the end of the five week treatment operation, the total volume of effluent water was respectively 2.230 and 5.184 litres from One and Two Process Approach experiments. The former, whose effluent flow had dried up by the end of the first week, had an ultimate discharge volume which was nearly forty percent of the latter. The lower total effluents in the One Process experiments were attributable to the non irrigation of the test cell causing the soil specimen to progressively dry up (Section 5.1b). The total volume of effluent water discharged by the control experiments was only 0.7 litres.

Additionally, during the investigations, the effluent discharges from the One and Two Approach experiments were initially observed to be milky due to the presence of suspended solids. Results in the Figure 5.40 show the cumulative mass of suspended solids measured from the two electrokinetic process effluents. Higher quantities of the fine solids were transported with the effluents in the initial stages of the two treatment scenarios. Since a third of the kaolin at the cathode area of respective cells appeared to have been eroded during this period, the bulk of the dissolved and suspended solids were considered to be kaolin clay particles from the cathode area in the soil chamber.

Kaolin contains quartz (SiO_2) and diaspore (Al_2O_3) (refer to Table 4.1). At equilibrium with water, kaolin is metastable at room temperature, converting completely to equal amounts of quartz and diaspore. However, when there is a change in the pH from its natural buffered value of 6.8, the mineral becomes less stable in its solid form. This manifests itself as a change in reaction rate and dissolution becomes more obvious. During the electrokinetic process, the electrons discharged at the cathode, hydrolyse the

water into hydrogen and hydroxyl ions (Equation 2.2). The hydrogen ions are neutralised by the electrons to make hydrogen atoms and these combine in pairs to evolve as molecular hydrogen gas. This leaves hydroxyl ions behind causing the pH to rise. The net result of this is that the equilibrium between the solids and liquid is displaced and to restore equilibrium, diaspore dissolves according to Equation 5.1. In general, besides temperature and pressure, the reaction equilibrium in Equation 5.1 moves to the right with increases in pH.



The dissolution of kaolin observed in this study concurred with work by Tyrer (2006). Tyrer studied the relative stability fields for kaolin by adding either hydrochloric acid or sodium hydroxide to the mix water for 10 moles of kaolin (about 2.5 kilos) and 1 litre of mix “water”. When 1 milli mole of sodium hydroxide was added to the 1 litre of mix water, then mixed with 10 moles of kaolin and allowed to equilibrate, the ionic strength at equilibrium went up by a factor of a thousand. In effect, the increase in pH drove diaspore into solution, leaving the quartz behind. This is properly illustrated in Figure 5.41, where the Y axis denotes the moles of mineral precipitated (positive values) or dissolved (negative values) as 10 moles of kaolinite equilibrates with 1 litre of water, and on the X axis, pH is expressed as equilibrium pH of the slurry after reaction with either hydrochloric acid or sodium hydroxide. The results indicate that at high pH, diaspore dissolves leaving the quartz behind. The opposite occurs when the pH conditions are reduced low enough.

In this study, of the two treatment processes, the anode irrigated cell discharged more solids in the effluent. It produced 281g compared to 204g of the One Process experiment. Beside the pH changes, the cells with the irrigating water produced higher solution mass transport due to the higher volumetric effluent flow. Larger volumetric water flows at the cathode enhanced the movement of the dissolved and fine clay minerals past the filter system into the effluent chamber.

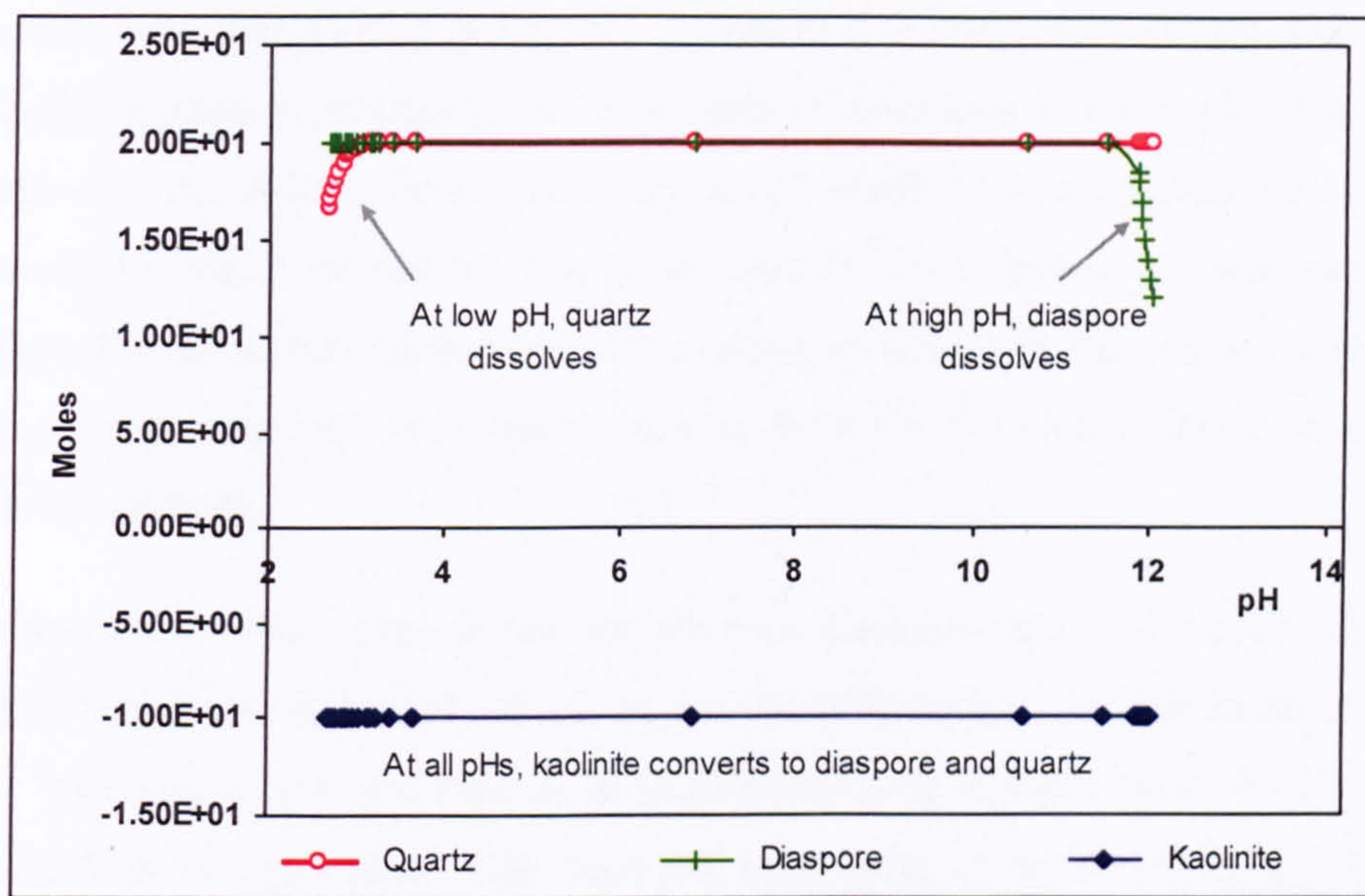


Fig 5.41 *Dissolution / Precipitation of Mineral Phases during Equilibration of Kaolinite with Water (After Tyrer, 2006)*

(b) Contaminant Mass and pH

Once the concentration of the Zn^{2+} in the effluent water specimens and the dispersed solids was measured using the atomic absorption spectrometer according to the procedures in Section 4.3.2, the respective metal contaminant masses were calculated using Equation 5.2 for the effluent water and Equation 5.3 for the suspended solids. The details of the computations appear in Tables A5.4 and A5.5 in the appendix.

$$\text{Contaminant Mass in Effluent Water (mg)} = C_L \times V_L \quad 5.2$$

$$\text{Contaminant Mass in Suspended Solids (mg)} = C_S \times V_S \quad 5.3$$

Where:

C_L - was the concentration of Zn^{2+} in liquid fraction of the effluent (in mg/L),

V_L - was the corresponding volume of liquid fraction of the effluent (in L),

C_S - was the concentration of Zn^{2+} in suspended solids (in mg/kg), and

M_S - was the mass of suspended solids (in kg).

The results were then plotted in Figure 5.42 where it is demonstrated that, during all the investigated treatment processes, Zn^{2+} were able to continuously leach out of the test soil materials with the effluent flow. Generally, much smaller concentrations were measured past the first week of treatment. The continuous Zn^{2+} presence in the effluents, was an indication that the metal cations were able to advance with both the seepage water (in the control experiments) and with electroosmotic flow (in the electrokinetic experiments) towards the cathode.

Furthermore, the same figure shows that for each electrokinetic experiment effluent, Zn metal recovery in the dispersed solids was considerably higher than that in the discharged water. This was despite the bulk of the discharge being effluent water as illustrated in Table A5.6 in the appendix. The high pH (averaging at about 10) arising from the abundance of hydroxyl ions generated at the cathode (Section 5.4) caused some Zn cations (already attracted at the cathode side by electromigration) to come out of solution as hydroxides while some cations adsorbed on to the fine clay suspensions. It is evident from Figure 5.43 that as the pH increases beyond 7, the solubility of the zinc hydroxide decreases steadily.

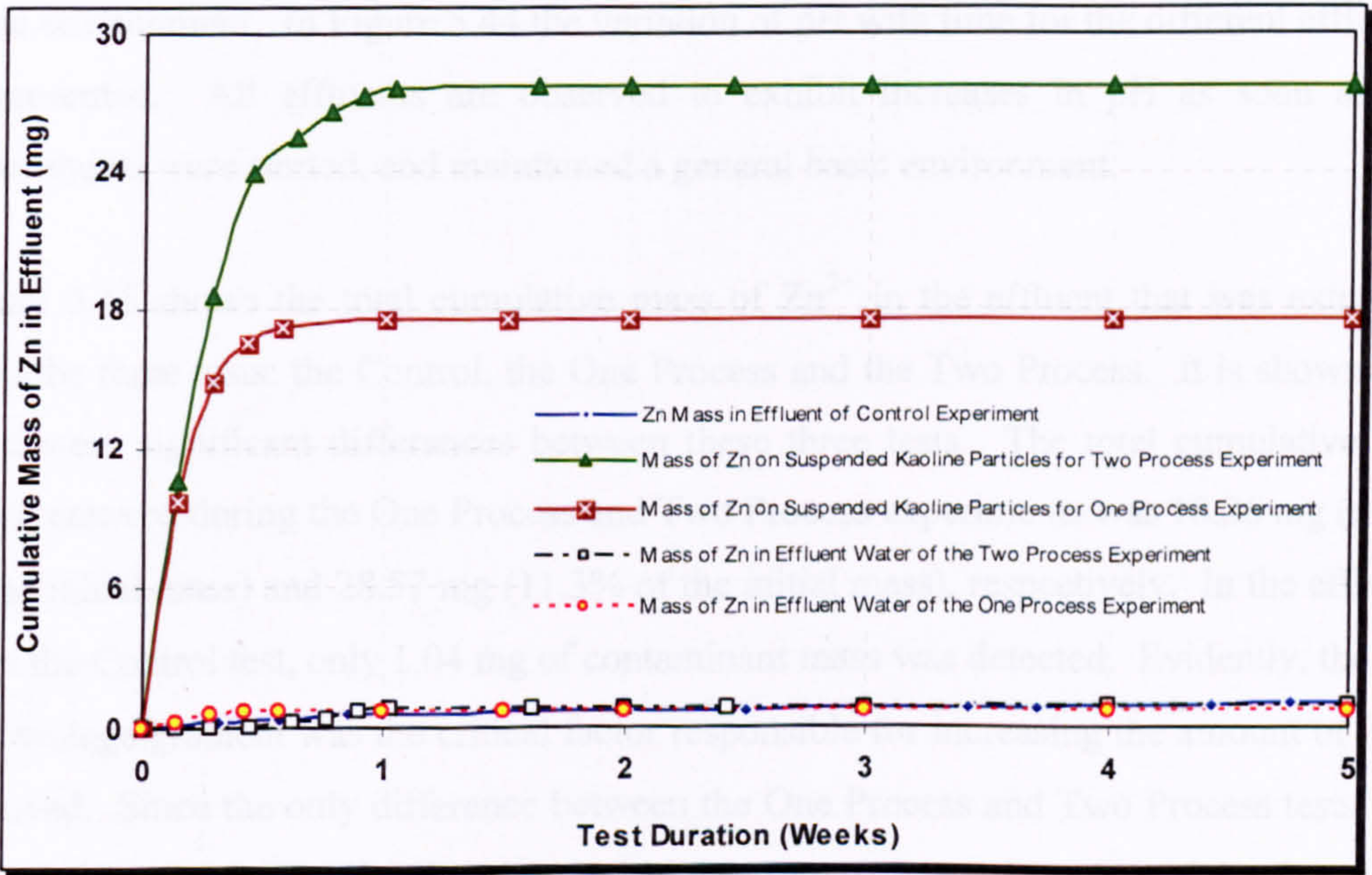


Fig 5.42 Cumulative Mass of Zinc Ions in Effluent Water and Suspended Solids for the Different Treatment Processes

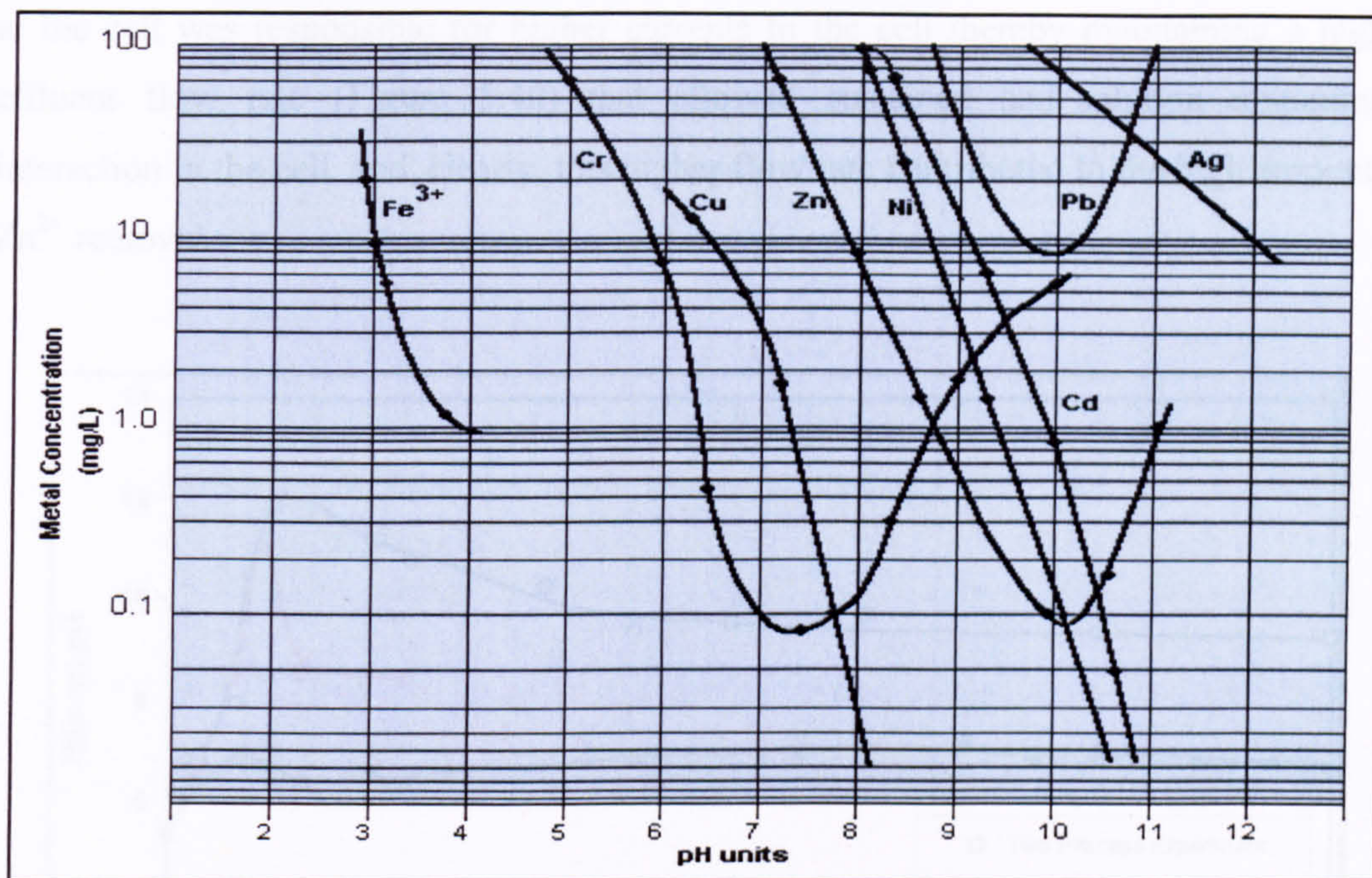


Fig 5.43 Metal Hydroxide Solubility Curve Showing the Solubility of the Common Heavy Metal Ions and their Respective Solubility versus pH (After, Hoffland Environmental, 2005)

Additionally, as already shown in Figure 2.12 metal adsorption on to kaolin is higher in a basic environment. In Figure 5.44 the variation of pH with time for the different effluents is presented. All effluents are observed to exhibit increases in pH as soon as the experiments were started, and maintained a general basic environment.

Figure 5.45 shows the total cumulative mass of Zn^{2+} in the effluent that was extracted from the three tests: the Control, the One Process and the Two Process. It is shown that there were significant differences between these three tests. The total cumulative Zn mass removed during the One Process and Two Process experiments was 18.26 mg (6.7% of the initial mass) and 28.57 mg (11.3% of the initial mass), respectively. In the effluent from the Control test, only 1.04 mg of contaminant mass was detected. Evidently, the use of a voltage gradient was the critical factor responsible for increasing the amount of Zn^{2+} removed. Since the only difference between the One Process and Two Process tests was the irrigation of the anode, the observed higher removal (nearly twice of the former in terms of percentage of initial mass) is largely attributed to the higher cell moisture contents and electroosmotic flow towards the cathode caused by the continuous availability of water to the test cell. As seen in Figure 5.9, the continuous supply of water

to the cell was responsible for higher currents in the cell thereby maintaining a higher effluent flow rate (Figure 5.40) that allowed sustained soil–solution–contaminant interaction in the cell, and, clearly, this higher flow rate contributed to the high amount of Zn^{2+} removal.

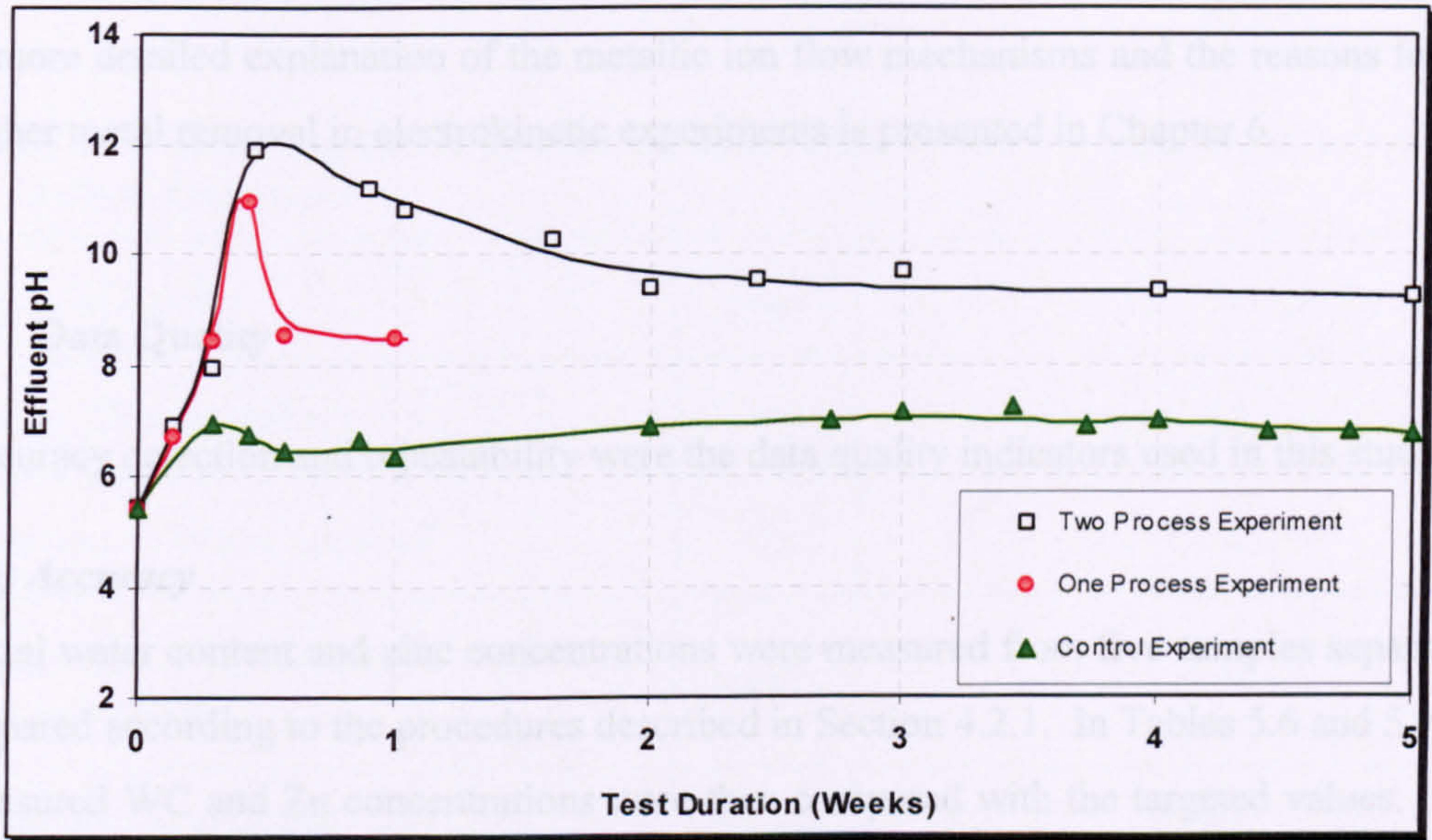


Fig 5.44 Variation of Effluent pH with Test Duration

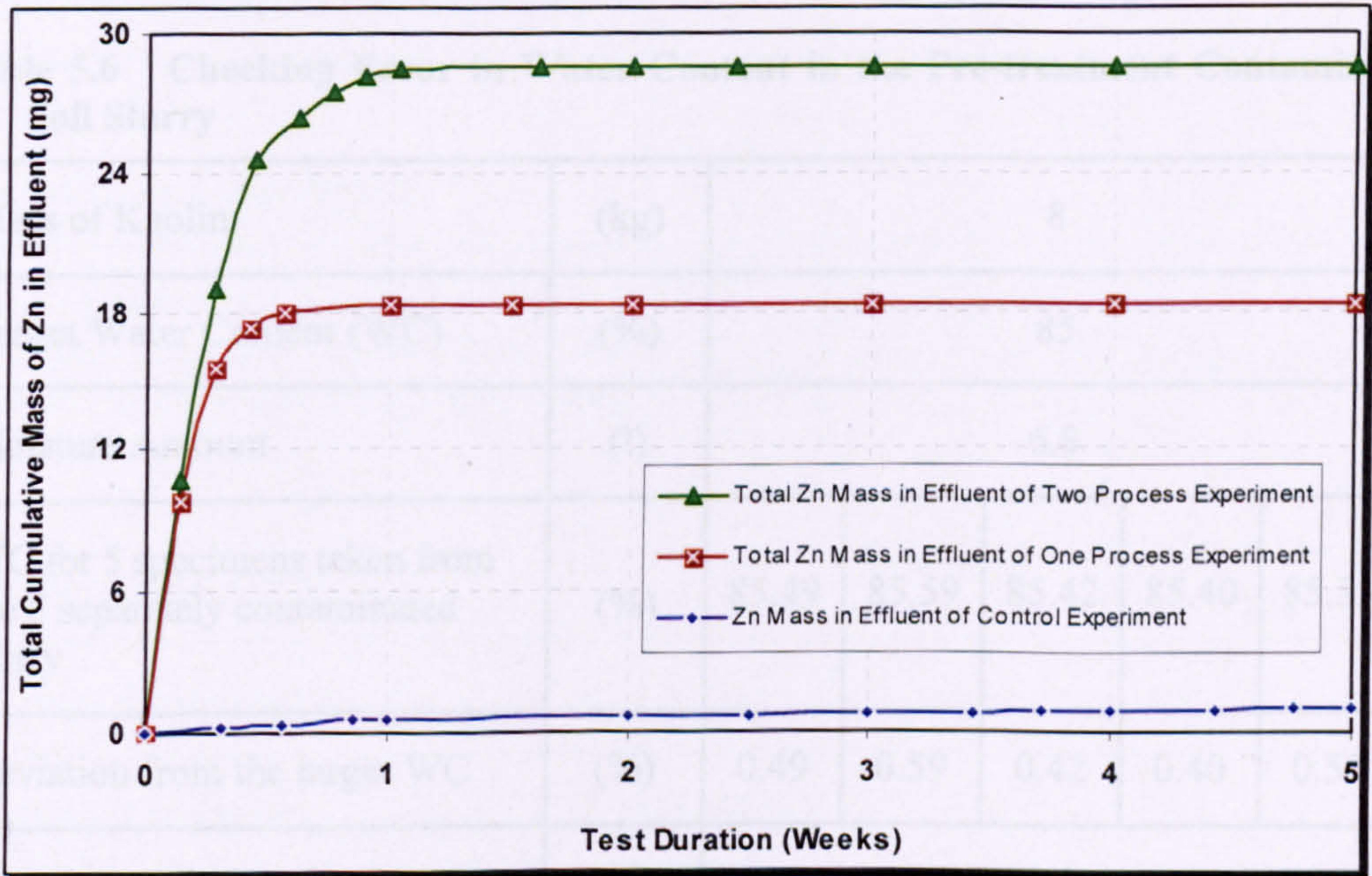


Fig 5.45 Total Cumulative Mass of Zinc Ions Removed from the Different Treatment Processes

In all three operations, the total mass of the heavy metal ions, extracted with the effluent from the specimen soil, was highest at the start of the experiment and reduced gradually with experiment duration. Over 50% and 90% of the total metal contaminant recovered respectively in the effluent from the control and the electrokinetic processes were extracted in the first week of investigation.

A more detailed explanation of the metallic ion flow mechanisms and the reasons for the higher metal removal in electrokinetic experiments is presented in Chapter 6.

5.6 Data Quality

Accuracy detection and repeatability were the data quality indicators used in this study.

(a) Accuracy

Initial water content and zinc concentrations were measured from five samples separately prepared according to the procedures described in Section 4.2.1. In Tables 5.6 and 5.7 the measured WC and Zn concentrations were then compared with the targeted values. It is demonstrated in Table 5.6 that the deviation from the target WC ranged between 0.4% and 0.6% resulting to an average error of 0.5%.

Table 5.6 Checking Error in Water Content in the Pre-treatment Contaminated Soil Slurry

Mass of Kaolin	(kg)	8				
Target Water Content (WC)	(%)	85				
Moisture Amount	(l)	6.8				
WC for 5 specimens taken from the 5 separately contaminated slurry	(%)	85.49	85.59	85.42	85.40	85.53
Deviation from the target WC	(%)	0.49	0.59	0.42	0.40	0.53
Average Deviation (Error)	(%)	0.5				

Table 5.7 shows sample results of the Zn concentration used for accuracy evaluation. Results show that the target contaminant concentrations were not identically achieved. In all samples, the percent recovery was greater than 100% - measurements were between 101% and 108%. Nonetheless, almost all (four out of the five) samples fell within a standard deviation of the measured values.

Table 5.7 Checking Error in Zinc Concentration in the Contaminated Soil Slurry before Treatment

Mass of Kaolin	(kg)	8				
Target Water Content	(%)	85				
Amount of Water required	(l)	6.8				
Required ZnCl ₂ Electrolyte Concentration	(mg/l)	100				
Mass of ZnCl ₂ added	(mg)	680				
Zn in 680 mg of ZnCl ₂	(mg)	326.23				
Total dry mass of the soil and ZnCl ₂	(kg)	8.0007				
Expected Zn Concentration	(mg/kg)	$\frac{326.23}{8} = 40.78$				
Zn concentration determined from 5 separate samples taken from the contaminated slurry and tested using AAS	(mg/kg)	44.01	42.12	41.18	43.48	43.13
Percentage Recovery	%	107.9	103.3	101.0	106.6	105.8
Average Deviation (Error)	(%)	4.9				
Standard Deviation	(mg/kg)	2.77				

(b) Repeatability

Table 5.8 to 5.11 show the comparison of weekly electrical currents for the different experiments. It is illustrated that at any reference period, the obtained weekly results were similar. The average maximum deviation from the mean weekly current in all test conditions is under 10%.

Table 5.8 Comparison of Weekly Currents for the 5 Experiments Conducted without Flushing at Anode

Duration (Weeks)	Weekly Current Reading (A)					Average Current (A)	Maximum Deviation from Average (A)	Percentage Deviation (%)
	1 Week Expt.	2 Week Expt.	3 Week Expt.	4 Week Expt.	5 Week Expt.			
0	0.048	0.047	0.049	0.049	0.049	0.04830	0.0013	2.69
1	0.007	0.007	0.008	0.007	0.008	0.00746	0.0005	6.16
2		0.003	0.004	0.004	0.003	0.00350	0.0005	14.18
3			0.003	0.002	0.002	0.00253	0.0001	3.95
4				0.002	0.001	0.00141	0.0004	29.20
5					0.000	0.00000	0.0000	0.00
Average Deviation (Error)							0.0005	9.37

Table 5.9 Comparison of Weekly Currents for the 5 Experiments Conducted with Flushing at Anode for H = 150mm

Duration (Weeks)	Weekly Current Reading (A)					Average Current (A)	Maximum Deviation from Average (A)	Percentage Deviation (%)
	1 Week Expt.	2 Week Expt.	3 Week Expt.	4 Week Expt.	5 Week Expt.			
0	0.048	0.047	0.051	0.049	0.047	0.04840	0.0026	5.37
1	0.012	0.012	0.014	0.011	0.013	0.01230	0.0017	13.82
2		0.010	0.009	0.009	0.010	0.00950	0.0005	5.26
3			0.006	0.006	0.007	0.00633	0.0007	10.53
4				0.005	0.006	0.00550	0.0005	9.09
5					0.005	0.00500	0.0000	0.00
Average Deviation (Error)							0.0009	7.35

Table 5.10 Comparison of Weekly Currents for the 5 Experiments Conducted with Flushing at Anode for H = 300mm

Duration (Weeks)	Weekly Current Reading (A)					Average Current (A)	Maximum Deviation from Average (A)	Percentage Deviation (%)
	1 Week Expt.	2 Week Expt.	3 Week Expt.	4 Week Expt.	5 Week Expt.			
0	0.096	0.094	0.096	0.098	0.099	0.09660	0.0026	2.69%
1	0.020	0.018	0.020	0.022	0.025	0.02095	0.0031	15.02%
2		0.012	0.015	0.015	0.017	0.01448	0.0030	20.59%
3			0.010	0.010	0.012	0.01051	0.0010	9.34%
4				0.008	0.009	0.00840	0.0006	7.14%
5					0.007	0.00700	0.0070	0.00%
Average Deviation (Error)							0.0029	9.13%

Table 5.11 Comparison of Weekly Currents for the 5 Experiments Conducted with Flushing at Anode for H = 150mm and Replenished Drainage Channels

Duration (Weeks)	Weekly Current Reading (A)					Average Current (A)	Maximum Deviation from Average (A)	Percentage Deviation (%)
	1 Week Expt.	2 Week Expt.	3 Week Expt.	4 Week Expt.	5 Week Expt.			
0	0.017	0.016	0.017	0.017	0.016	0.01650	0.0005	3.03%
1	0.009	0.009	0.008	0.009	0.009	0.00896	0.0006	6.25%
2		0.004	0.004	0.005	0.004	0.00413	0.0007	16.36%
3			0.003	0.004	0.004	0.00347	0.0005	13.46%
4				0.003	0.003	0.00320	0.0002	6.25%
5					0.002	0.00200	0.0000	0.00%
Average Deviation (Error)							0.0004	7.56%

Zinc concentration and water content measurements from replicate five weeks experiments were taken from the One Process and Two Process samples. Precision of the results was expressed as relative percent difference (RPD) from the average value (Equation 5.4).

$$\text{RPD} = \frac{\text{Deviation}}{\text{Mean}} \times 100 \quad 5.4$$

Tables 5.15 and 5.16 show the results and precision calculations. It is observed that in almost all duplicate samples (24 out of 28), the RPD was less than 40. The reference value of 40 was specified by Acar et al. (1997) in their research as the target maximum

Table 5.12 Comparison of Results from Two 5 Weeks Experiments Conducted without Flushing at Anode for H = 150mm

Zinc Concentration						
Location along Cell		Measured Concentration (mg/kg)		Mean Concentration (mg/kg)	Deviation (+/- mg)	Relative Percentage Difference from Mean (%)
		Test 1	Test 2			
Top	Anode	44.28	16.94	30.61	13.67	44.7
	(1/4)L	8.24	10.05	9.14	0.91	9.9
	(1/2)L	11.34	18.59	14.96	3.63	24.2
	(3/4)L	141.43	148.61	145.02	3.59	2.5
Middle	Anode	14.23	11.15	12.69	1.54	12.1
	(1/4)L	6.47	12.64	9.55	3.09	32.3
	(1/2)L	26.85	23.31	25.08	1.77	7.1
	(3/4)L	215.31	173.44	194.37	20.93	10.8
	Cathode	74.62	65.83	70.23	4.39	6.3
Bottom	Anode	16.28	21.06	18.67	2.39	12.8
	(1/4)L	5.14	7.41	6.28	1.13	18.1
	(1/2)L	15.69	18.47	17.08	1.39	8.1
	(3/4)L	63.00	66.33	64.66	1.67	2.6
	Cathode	37.95	38.06	38.00	0.06	0.1
Average Water Content						
Location along Cell		Measured Water Content (%)		Mean WC (%)	Deviation (%)	Relative Percentage Difference from Mean (%)
		Test 1	Test 2			
Middle	Anode	35.20	33.90	34.55	0.65	1.9
	(1/4)L	33.07	34.23	33.65	0.58	1.7
	(1/2)L	34.60	33.97	34.29	0.31	0.9
	(3/4)L	34.80	34.46	34.63	0.17	0.5
	Cathode	34.64	33.85	34.25	0.39	1.1

allowed RPD. Review of their work, however, did not reveal any explanation on how the figure was arrived at.

Table 5.13 Comparison of Results from Two 5 Weeks Experiments Conducted with Flushing at Anode for H = 150mm

Zinc Concentration

Location along Cell		Measured Concentration (mg/kg)		Mean Concentration (mg/kg)	Deviation (+/- mg)	Relative Percentage Difference from Mean (%)
		Test 1	Test 2			
Top	Anode	6.32	74.59	40.45	34.14	84.4
	(1/4)L	6.14	10.25	8.20	2.05	25.0
	(1/2)L	8.34	9.12	8.73	0.39	4.4
	(3/4)L	13.90	7.97	10.94	2.96	27.1
Middle	Anode	5.38	10.83	8.11	2.72	33.6
	(1/4)L	8.29	8.68	8.48	0.20	2.3
	(1/2)L	4.79	10.52	7.66	2.87	37.4
	(3/4)L	12.51	9.98	11.24	1.26	11.2
	Cathode	53.31	62.53	57.92	4.61	8.0
Bottom	Anode	5.47	109.47	57.47	52.00	90.5
	(1/4)L	7.82	8.20	8.01	0.19	2.4
	(1/2)L	8.31	9.19	8.75	0.44	5.0
	(3/4)L	3.19	9.69	6.44	3.25	50.5
	Cathode	58.83	44.77	51.80	7.03	13.6

Average Water Content

Location along Cell		Measured Water Content (%)		Mean WC (%)	Deviation (%)	Relative Percentage Difference from Mean (%)
		Test 1	Test 2			
Middle	Anode	75.38	75.70	75.54	0.16	0.2
	(1/4)L	57.57	49.96	53.77	3.80	7.1
	(1/2)L	52.15	46.87	49.51	2.64	5.3
	(3/4)L	55.01	52.19	53.60	1.41	2.6
	Cathode	55.14	55.04	55.09	0.05	0.1

5.7 Summary of Findings

Overall the results of the study revealed that:

(a) Electrical Current

- 1) In all test cases, the measured electrical current decreased with time. In the One Process Approach (closed anode conditions - no free access to water), the reduction was non linear in the first two weeks but became linear in the last three weeks of experimentation. However in all Two Process Approach investigations (open anode conditions - having free access to water), the current into the test cells dropped in a non linear trend from start to finish.
- 2) In both open and closed anode conditions, electrical power decreased rapidly in the first week of treatment before the reduction stabilised in the following weeks.
- 3) Operating an intermittent electrical current system – in which the current was applied at predetermined 24 hours on / 24 hours off intervals during electrokinetic treatment - resulted in lower reductions in the weekly current than systems conducted with a continuous direct current. This confirmed that the periodic interruption of the power supply, during treatment, results in lower power consumption.
- 4) Generally, in terms of weekly test current values, the respective periodic current values obtained with open anode investigations were higher than those obtained with the closed anode. The exception was with specimens aligned with three waterlogged-drainage channels, replenished with deionised water every after 24 hours during treatment. These had the lowest initial electrical currents of all the investigations. However from the end of the first week onwards, the current values of the closed anode had reduced to values lower than those of replenished channel investigation.
- 5) While keeping all other parameters constant, doubling the soil specimen depth resulted in the weekly electrical current into the test cell approximately doubling.

(b) Water Content

- 1) The WC at any specified section within the soil specimen mass generally decreased with time during the electrokinetic process of both closed (electrokinetic only) and open anode (combined soil flushing and electrokinetic) conditions. The highest drop in soil pore water occurred during the first week of cleaning, with subsequent weekly decreases in WC values falling with increase in test duration.

For the open anode conditions, however, the reductions in WC were minimal beyond the second week of treatment. That is, as the experiments progressed after week 2, residual WC values were being established at the respective sections of the test specimens.

- 2) The periodic WC along the soil mass of the open anode experiments were higher than those treated under the closed anode conditions. The results confirmed that the constant water irrigation into the anode end of the test samples, during the electrokinetic process, was responsible for the higher cell water contents.
- 3) During the investigations, the WC within the soil specimens of the closed anode cells was nearly the same irrespective of the position in the cell. While in the open anode cells, the highest pore water was at the anode, and typically reduced with increased distance towards the centre of the cell before slightly increasing in the cathode direction. The higher WC at the anode, in the latter experiments, was a result of the constant water supply flushing into the electrode section during the five weeks of testing.
- 4) The WC trends exhibited by the 150mm high water flushed samples were generally comparable to those of the 300mm high samples treated under identical test conditions. Doubling the sample height did not appear to significantly change the WC characteristics especially in the middle and bottom layers of the cell.
- 5) Interrupting the electrical current periodically (24 hours on and 24 hours off) during treatment resulted higher water content along the specimen length than in the continuous direct current conditions. Higher periodic WC values were also obtained when the soil length was aligned with waterlogged-drainage channels aligned equidistant along the soil length.

(c) Zinc Removal

- 1) In both closed and open anode investigations, application of a low-voltage current through the soil specimens caused the Zn^{2+} concentration on the anode side of the test cells to drop while effecting a simultaneous increase in metal contamination on the cathode side. This created a metallic concentration gradient along the test soil length with falling contaminating cations concentration at the anode but rising levels towards the cathode side. This indicated that the stream of the target metallic ions did migrate, under the influence of the applied electric field, in the direction of the cathode.

Consequently, the cathode section and its close proximity were the most contaminated region of the cell throughout testing. For the closed cells experiments, the heavy metal pollutant accumulated highest at a quarter the distance from the cathode while under the open anode conditions, it was observed at the cathode. The final Zn concentration at the former was up by one and a half times the initial amount and by a fifth at the later.

- 2) In both investigations, the highest periodic removal of the metal ions along the cell was achieved in the first two weeks of treatment. By this period alone, the metal concentration in the anode half of the cell of the closed and open anode conditions tests had respectively dropped by 65 and 80%.
- 3) Over the five weeks testing programme the combined treatment operation of soil flushing and electrokinetic, produced superior clean up results than treatment with electrokinetic only. The later removed over 80% of the metal in more than three quarters of the test cell while the removal efficiency was 70% in only half the cell of the closed anode.
- 4) With the exception of the results at the bottom of the cathode side (from $\frac{1}{2}L$ to the cathode), the general trends of the spatial and temporal variations in Zn^{2+} concentrations along two test specimens, of difference heights and treated under the same conditions, were consistent with each other. At the bottom of the cathode side, the larger cell (twice the height of the smaller cells) produced higher metal ions concentrations.

The average treatment results, though, established that in spite of this difference, the ultimate heavy metal exclusion efficiencies approximated to the same values in both

investigations. Doubling the height, while keeping all other variables constant, did not appear to significantly affect the overall metal migration characteristics during the joint application of electrokinetic and soil flushing processes.

- 5) Conducting current intermittence intervals of 24 hours on and 24 hours off during cleaning up, achieved identical removal efficiencies as those obtained with uninterrupted electrical DC supply at the anode and $\frac{1}{4}L$. At $\frac{1}{2}L$ and $\frac{3}{4}L$ the metal removal was much lower, while the metal ions quantity increased at the cathode by 1.5 times that of the tests run under continuous currents.

Thus the benefit of reduced power consumption through periodic current interruption (of 24 hours on and 24 hours off) did not result in an improved metal removal from the test specimens.

- 6) Addition of three waterlogged-drainage channels aligned equidistant along the soil length, and whose water was replenished every after 24 hours, improved the metal removal at the cathode area. The final average Zn concentration at this position fell by 25%. Elsewhere in the cell, however, lower metal removals than specimens tested without the replenished drainage chambers were realized.

(d) Effluent

- 1) During both control (soil flushing only) and electrokinetic treatments, the effluent flow rate was highest at the start but dropped considerably with increase in experiment duration.
- 2) Applying a low voltage current across the soil specimen resulted in much higher effluent flow volumes than simply allowing water to flush unenhanced across the soil.
- 3) Zn^{2+} were leached out of the soil together with the effluent water during both soil flushing and electrokinetic processes. The highest metal contaminant mass was extracted in the initial stages of the treatments when electrical current was also highest.
- 4) Applying a current across the test specimen generated substantially higher metal cations in the purge water.

5.8 Concluding Remarks

This Chapter has provided results of bench-scale experiments performed to investigate the effectiveness of using EKGs in electrokinetic remediation of fine grained soils contaminated with heavy metals under closed and open anode situations. In the process, different physical characteristics such as: effects of water flushing, sample depth, intermittent current and addition of replenished draining chambers along the cell length have been explored. The trends and changes brought about in the soil specimens during the different applied treatment conditions have all been presented in depth in this chapter. However, the relationship between the electrical current and water content, water content movement and Zn^{2+} movement as well as pH and Zn^{2+} concentration along the test specimens needed to be examined further. Such analysis would provide a better understanding of the mechanisms by which the changes presented in this chapter have been brought about. Chapter 6 explores all these further.

ANALYSIS AND DISCUSSION OF RESULTS

6.0 Introduction

The objective of this chapter is to analyse and discuss data already presented in Chapter 5 as well as to put the research findings into context. The chapter initially begins by explaining the temporal electrical current trend observed during the experiments. The mathematical relationship between the current density and test duration is established. The spatial water content changes in the test soil specimens are examined and evaluated. The development and movement of pH gradients during electroosmosis are also investigated since it was found that pH gradients play an important role in contaminant removal. Then, the metal contaminant removal for different test environments and their extraction efficiencies are discussed in great detail by looking at: the relationships between the electrical current and pore water movement; current consumption and Zn ions movement; as well as pH and Zn ion concentrations along the test specimens. The culmination of the discussion, are recommendations for improving the performance of the bench-scale model used in the study. The advantages of this model, over previous ones used by other researchers in electrokinetic remediation of metal contaminated soils, are given.

In each section, interim conclusions are drawn in order to summarise the key findings of the study.

6.1 Electrical Current

6.1.1 Discussion of Results

Figure 6.1 shows that the average current values for all the test cases exhibited a similar trend. Generally, the current decreased rapidly during the first week, before the drops stabilised in the following weeks. The voltage gradient in all the continuous direct current supplied investigations was maintained at a constant value of 0.5V/cm.

When the contaminated water was originally added to the kaolin, the salts that were associated with the dry clay particles dissolved into the water to form a solution with

aluminium and silicate concentrations of $2.173\text{E-}09$ and $1.108\text{E-}04$ moles per kg respectively. This produced a pore solution with a high ionic strength. In addition, the ionic heavy metal contaminant ($7.33\text{E-}04$ moles of Zn^{2+} per litre) that was already dissolved in the water also contributed to increasing the ionic strength. Though other cations such as Na, Ca, K and Mg present in the clay minerals could influence the solution strength, their concentrations were not measured. This was because the impact of these cations to the solution strength was not in the scope of this study.

When the voltage was first applied, the current (or current density) was at its maximum in all the different test operations. This arose from the initial strong ionic concentration. All the ions were in solution since the specimens were saturated, specifically, there was no need for them to first mobilise to dissolve.

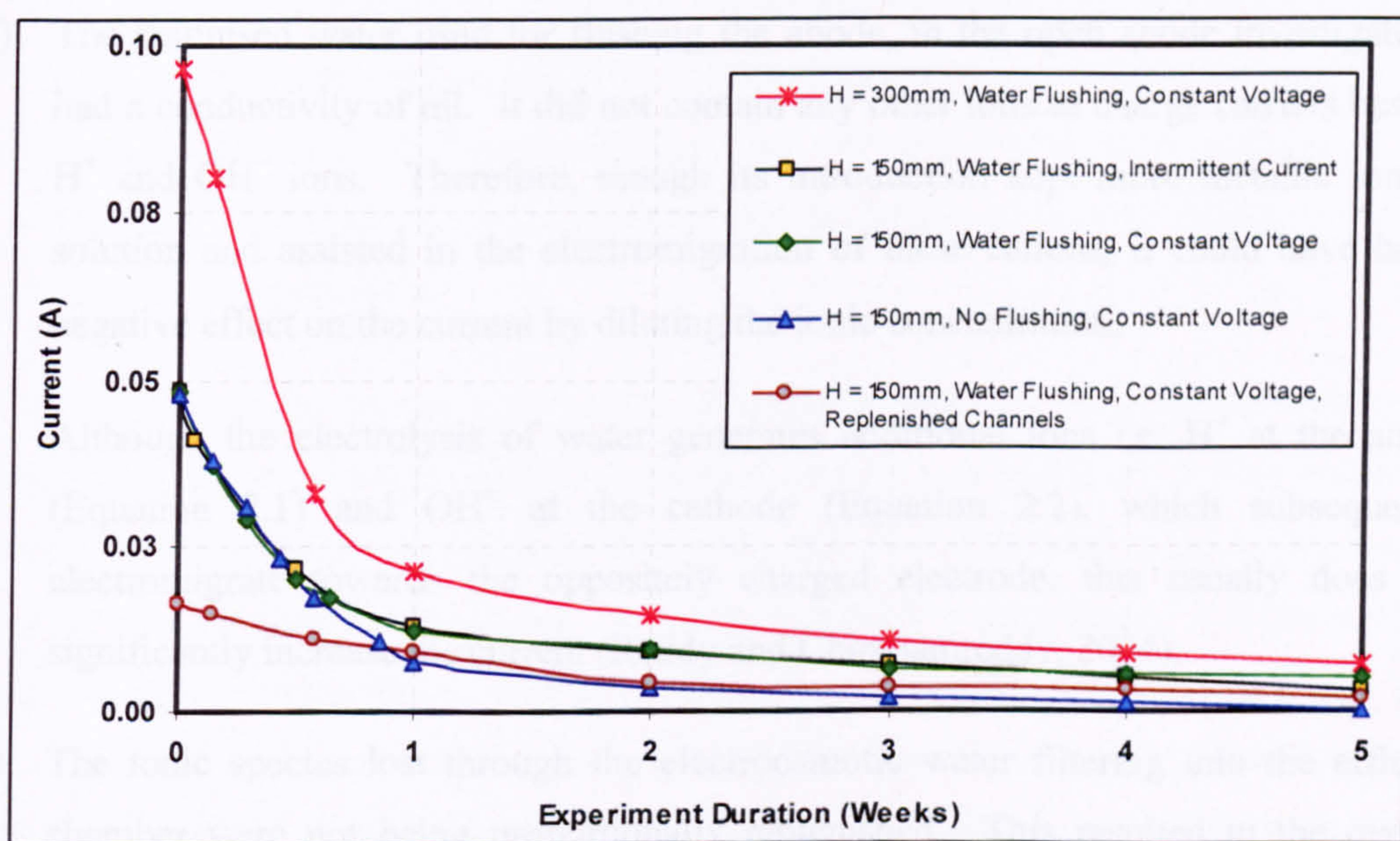


Fig 6.1 Comparison of the Average Temporal Current for the Different Test Characteristics

Then, the current started to decrease and to diminish over time. This was because of a number of reasons:

- 1) the cations and anions were electro migrating towards their respective electrode. This migration reduces the current (Reddy et al. 2002).

- 2) the products of the electrolysis reactions (refer to Section 2.3.2.1) could have reduced the current by neutralizing the migrating ions. For instance, H^+ ions (in the acid front) migrating towards the cathode could have been neutralized by OH^- ions (in the base front) migrating towards the anode, thereby forming high resistance water (Booher et al., 1997; Hamir, 1997) and reducing/ diluting the number of ions in solution.
- 3) Time-dependent pH changes due to the electrolysis reactions affected the current by causing changes such as mineral dissolution. Mineral dissolution was very evident at the cathode where the top third of the clay material around the cathode dissolved away. Dissolution of clay minerals was also observed by Acar and Gale (1992) at the cathode area when the pH there ranged between 7 and 9 units.
- 4) Chemical precipitation (refer to Section 2.3.2.4), which removes charged particles from solution, was demonstrated also in many results presented in the Chapter 5.
- 5) The deionised water used for flushing the anode, in the open anode investigations, had a conductivity of nil. It did not contain any other ions as charge carriers besides H^+ and OH^- ions. Therefore, though its introduction kept more metallic ions in solution and assisted in the electromigration of these cations, it could have had a negative effect on the current by diluting the ionic concentration.

Although the electrolysis of water generates additional ions i.e. H^+ at the anode (Equation 2.1) and OH^- at the cathode (Equation 2.2), which subsequently electromigrate towards the oppositely charged electrode, this usually does not significantly increase the current (Reddy and Chinthamreddy, 2004).

- 6) The ionic species lost through the electroosmotic water filtering into the effluent chamber were not being proportionally replenished. This resulted in the overall available mobile charge carriers constantly falling and getting depleted with time.
- 7) The gases being given off due to the electrolysis action at the electrodes; oxygen at the anode (Equation 2.1), and hydrogen at the cathode (Equation 2.2) as well as chlorine gas at the anode (Equation 3.1) all played a part.

The tiny bubbles formed around the electrodes are good insulators and increase the overall resistivity (Sah and Chen, 1998; Virkutyte et al. 2002). During treatment,

more gases bubbles were visually observed coming off at the electrodes in the early stages of the experiment, the intensity of which reduced with time.

- 8) Reactions at the anode causing low pH conditions can result in corrosion and dissolution of the electrode element (Vance, 2002). Electrical energy is lost during electrode degeneration. Studies by Pugh (2002), established that the EKG electrodes were not totally inert. In this study, however, electrodes inspected visually after the electrokinetic process did not show any evidence of significant physically disintegration.
- 9) Voltage lost at the soil – electrode interface. Monitoring conducted by Kulathilaka (2005) with voltage probes, and using the same EKG and soil material as was employed in this research, indicated that only 40 - 50% of the applied voltage was transferred to the soil during electrokinetic treatment. The rest was lost at the soil – EKG electrode interfaces. For this reason some researchers, such as Casagrande (1983), have suggested an empirical efficiency factor of 0.6 and 0.9 to account for the voltage loss at the soil – electrode interfaces. However the factor recommended, was based on the experience from field applications of electroosmotic treatment and not laboratory experiments.

In the beginning, the sample with the closed anode recorded the same current as the open anode one. Since both were partially saturated, and all ions mobilised in pore water, the electro ionic activity was bound to be the same. However with time, as the former sample was not being irrigated at the anode, the current started to reduce faster. It is obvious that because of the electroosmosis and electrolysis, the sample kept on losing the only pore solution it had as the investigation progressed. This caused the anode to start drying up. The ion mobility was consequently reduced as reducing water contents hindered electromigration. The specimen was more severely affected by pH changes, and the charged ions reduced faster than in the latter. It is conceivable that the replenishing water might have been beneficial because the resulting soil might have been more disperse, and this should make it easier for the ionic species to migrate through the pore network. The presence of additional water molecules may also have facilitated a greater amount of charged species hydration and ionic dissolution. This combination, therefore, resulted in a more sustained current for the flushed specimen than the unflushed one.

From the start, the measured currents in the 300mm high sample were double those for the 150mm specimens. According to Reddy et al. (2002), current is proportional to the ionic concentration. Since ions contribute to the electro strength (and conductivity) of the pore solution, doubling the specimen amount while keeping all other factors constant, the conductive ions sourced from the soil and contaminant were double resulting in a doubled ionic effect and a doubling of the current.

In investigations where current intermittence was exercised, the electrical current decreased at same rate as in the similar sized experiments operating with uninterrupted direct current. This indicated that there was no benefit of sustaining higher currents by using intermittent currents. During those intervals when current was off, no electromigration of charged species took place. However, as soon as the current was switched on, the ions almost spontaneously moved on.

From the start, the lowest current was recorded with test cells which had drainage channels aligned along the soil profile. In these particular investigations, each test cell had three 25mm thick drainage channels initially filled with deionised water and replenished every after 24 hours. Certainly, these test specimens had fewer charge carriers than the same sized cells without the interruption of the deionised water channels. Additionally, these channels were periodically being reloaded with pure water which had been deionised. This meant that the higher conductive contaminated solution was being replaced by the less conductive deionised water every so often.

6.1.2 Approximated Values

In order to be in position to estimate the electrical energy requirement for the different test cell conditions at any time during treatment, an attempt was made to develop a mathematical relationship from the current / test duration graph obtained experimentally.

Therefore, from Figure 6.1, the electrical current density was determined for each test category and plotted against the test duration in Figure 6.2. The current density was computed by dividing the current by the perpendicular (to the current flow direction) cross sectional area. The current density parameter was preferred over using electrical current parameters since the former is independent of the cell depth (if all other cell factors are kept constant).

Table 6.1 Mathematical Constants Values for the Relationship between Current Density and Test Duration

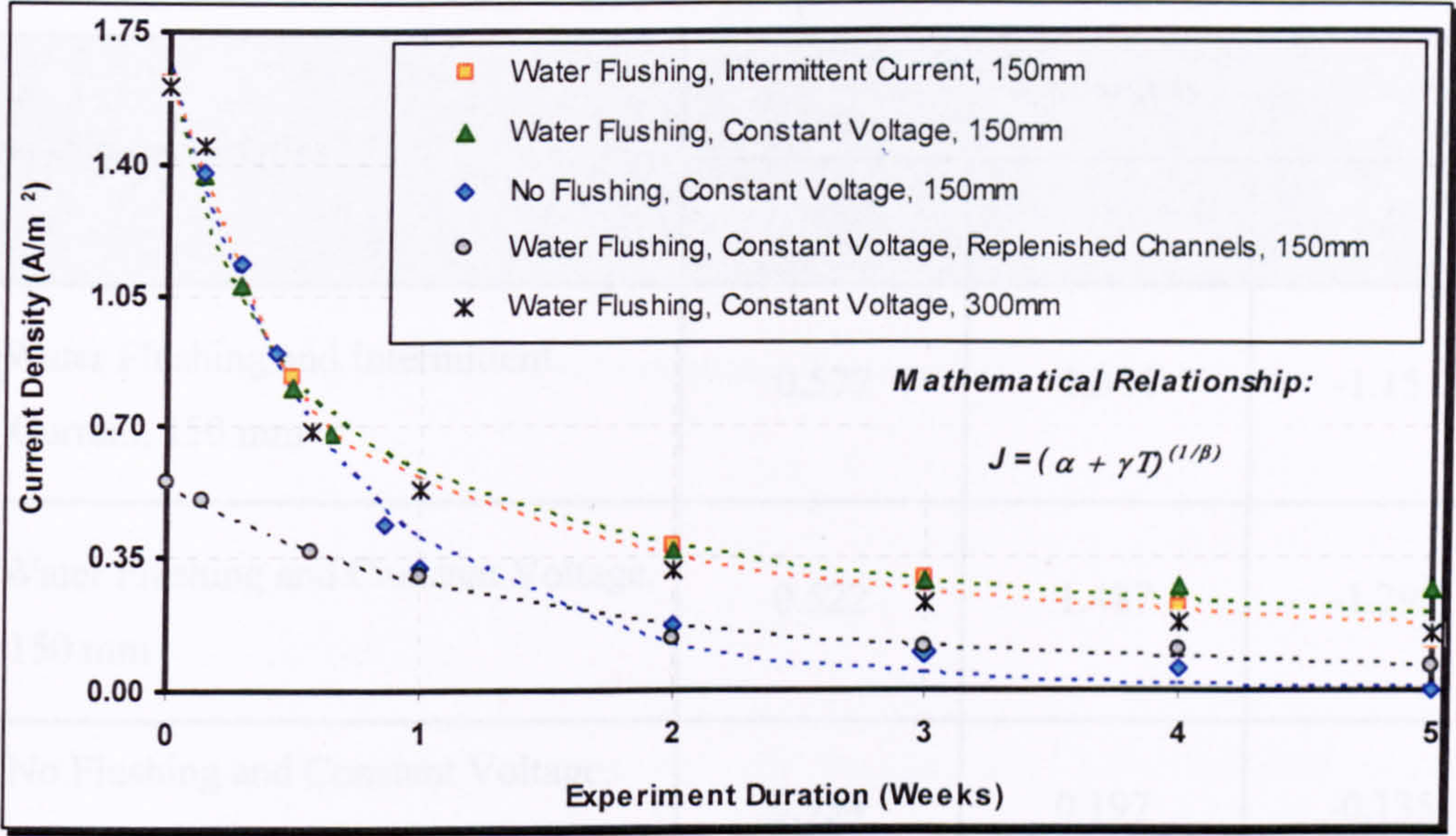


Fig 6.2 Relationship between Current Density and Experiment Duration Obtained Using Empirical Equations

It is observed in Figure 6.2, that the respective test current densities, at any time, could be approximated using a similar mathematical equation of the form shown in Equation 6.1. The respective mathematical relationships obtained using Equation 6.1, are represented by dotted lines in Figure 6.2 while the points are the corresponding values obtained experimentally.

Equation: $J = (\alpha + \gamma T)^{(1/\beta)}$ 6.1

Where:

J = Current Density, (A/m²)

T = Treatment Duration, (Weeks)

α , γ and β are constants whose values are a function of the test characteristics.

Table 6.1 gives the respective values of these constants based on the test conditions of this study.

Table 6.1 Mathematical Constants Values for the Relationship between Current Density and Test Duration

Test Characteristics	Constants		
	α	γ	β
1. Water Flushing and Intermittent Current, 150 mm	0.577	1.384	-1.151
2. Water Flushing and Constant Voltage, 150 mm	0.522	1.487	-1.292
3. No Flushing and Constant Voltage, 150 mm	0.934	0.197	-0.135
4. Water Flushing, Constant Voltage, and Replenished Channels, 150 mm	1.342	0.491	-0.481
5. Water Flushing and Constant Voltage, 300 mm	0.651	1.003	-0.837

It is clearly evident from above that the general trends of the mathematically engineered electrical current density / time relationship, for all the different test conditions, were consistent with the experimental values. And since the current densities for different test conditions could be approximated using the same equation by just changing the respective constants, implies that the format of Equation 6.1 could apply to any electrokinetic bench scale model characteristically the same as one used in this study.

The equation constants presented above are based on data from tests conducted using Type 3 EKGs as electrodes and with material characteristics and cell configurations presented in Chapter 4. To develop the equation constants so that they can be applied to any electrokinetic model requires further research. Those studies could involve a testing matrix with varying parameter inputs such as different voltage gradients, soil types, cell

sizes and configurations, electrode material types and spacing as well as different soil/contaminant characteristics. The resulting constants could be used to generate a design chart. Once produced, if the polluted soil material, contaminant characteristics and test conditions were known, the equation constants could be obtained from a single chart. Success in this would facilitate estimation of the power requirement for soil decontamination even before remediation starts. Also, if well developed, the equation would make it possible to make power estimates from a single laboratory test.

6.1.3 Interim Conclusions

The results have showed that:

1. During the electrokinetic treatment of the partially saturated soil samples contaminated with heavy metals, the electrical current was highest at the start of the process when the ionic concentration was at its highest. However due to many reasons listed in Section 6.1.1, this dropped gradually and consistently with test duration. The highest rate of decrease occurred during the initial period of treatment.
2. Test soil samples which were not irrigated at the anode lost current at a much faster rate than those that were. Flushing soil specimens with water at the anode maintained the electrical power over longer periods. However for an even more prolonged and enhanced electrical power, purging with ionised water would be recommended.
3. Doubling the specimen height doubles the specimen amount, consequently doubling the number of ions affected. Therefore, if all test parameters and test material characteristics are kept constant, doubling the specimen height doubles the current.
4. The relationship between the current density, J , and the test duration, T , was established to be of the form: $J = (\alpha + \gamma T)^{(1/\beta)}$. Where constants α , γ and β were a function of the test characteristics.

6.2 Water Content Movement

6.2.1 Discussion of Results

From all the respective temporal cell water content values presented in the previous chapter, general decreases in trend were observed especially in the first two weeks of treatment.

At the very start, when the electrokinetic treatment started, the range of electrokinetic processes discussed in Section 2.3.2 were initiated. Besides changes in soil pH (discussed in later sections) and losing moisture continuously due to electrolysis, there was an observed influx of pore water in the cathode region due to the electrical gradients. However, this flux of pore water and the insufficient supply of the pore fluid from the anode, due to the low permeability of the kaolin soil, caused suction to develop across the specimen (Reddy et al. 2002). This caused the sample to reduce in volume noticed by the development of cracks on the sample surface as well as vertical and horizontal movement of specimens during testing. This reduction in volume clearly caused the soil particles to get closer and the soil to become denser. This could have triggered a chain reaction illustrated in Figure 6.3:

- Densification has the effect of reducing the volume of the void space within the soil (porosity), increasing tortuosity and reducing the material permeability (Alshawabkeh, 2005). So changing the density changes these variables and accordingly the mobility of ions. According to Pamukcu (1997), decrease in the soil porosity, blocks the flow paths, and thus decreases the electroosmotic flow. It is possible that densification also causes the fines to clog the pore spaces, diminishing the flow paths which then impedes the movement of ions.
- Also, changes in physicochemical properties cause the electroosmotic permeability to drop (Steger et al., 2005). According to Acar and Gale (1992), electroosmotic permeability is time dependent and generally falls gradually during electrokinetics.

Since electroosmotic flow rate, Q (m^3/s), is expressed as (Mitchell, 1993) – (refer to equation 2.3):

$$Q = K_e \cdot \frac{V}{L} \cdot A$$

6.2

where k_e is the electroosmotic permeability of the soil ($\text{m}^2/\text{V}\cdot\text{s}$); V/L is the electrical potential gradient (V/m); and A is the cross-sectional area of the soil sample across which the potential difference is applied (m^2) - decreasing k_e would effectively result in decrease of Q , as V/L and A remained nearly constant throughout treatment.

- Similarly, the charged particle and ion migration rate would be constrained in conformity with the electroosmotic flow rate, Q .
- Electrical current dropping due to the slowed down movement of charged ions;
- Resulting in a reduced electrical current flow;
- Electroosmotic flow velocity reducing as a result;
- Lower electroosmosis would still cause suction due to insufficient supply of pore fluid – and the whole process would start all over again.

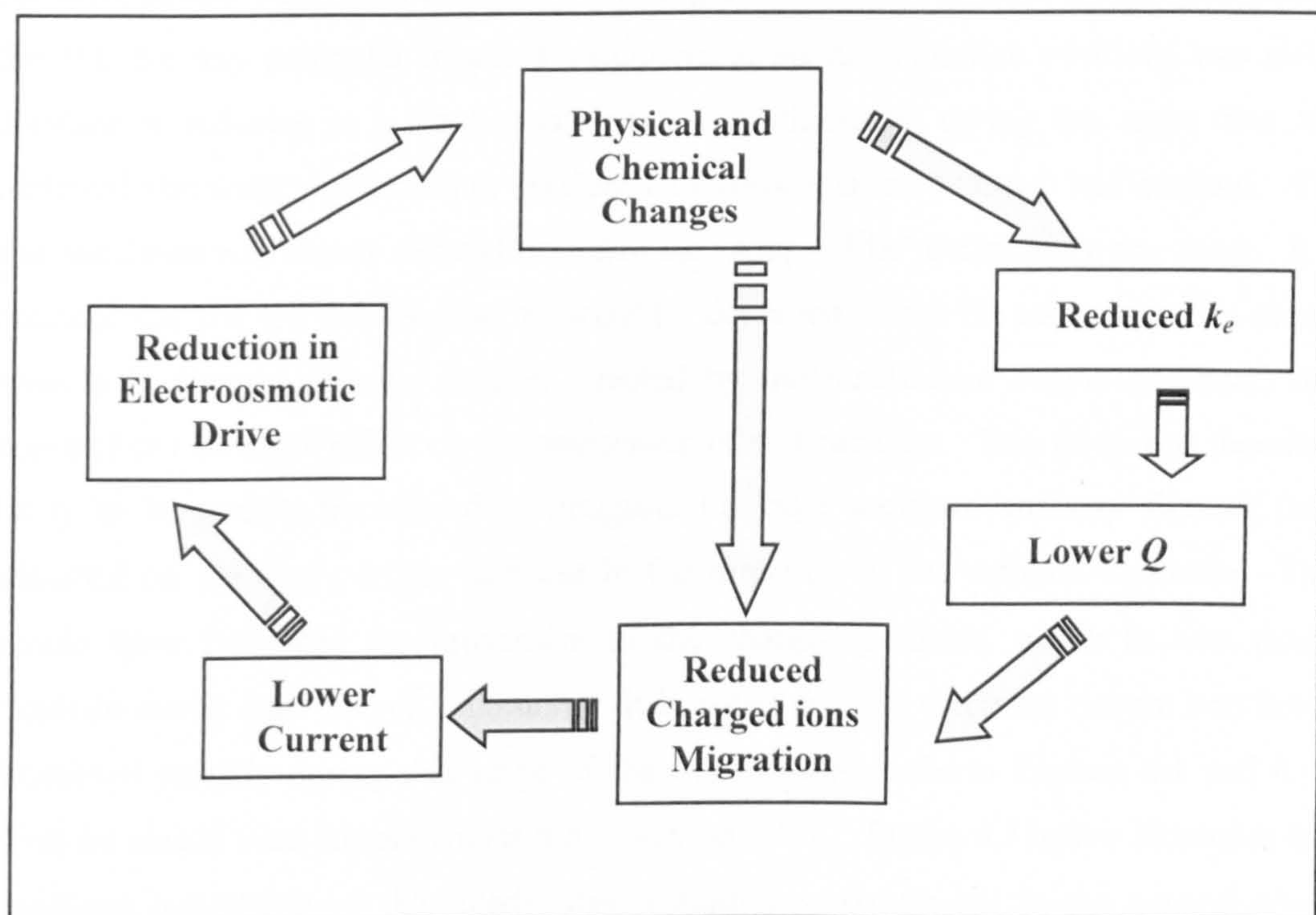


Fig 6.3 *Simplistic Hypothesis for the Initial Continuous Reduction of WC due to Physiochemical Changes*

Consequently, the WC, effectively, had to gradually reduce. The outcome was more pronounced in the unflushed specimen as there was no replacement water supplied from the anode compartment for what was in addition being lost into the effluent chamber due to electroosmosis.

The sharpest drops in WC for all test cases occurred in the first week, followed by the second. Since electrical current usually correlates to the electroosmotic drive (Reddy et al., 2002), high currents would create higher flow velocities and vice versa. It is evident in Figure 6.4, where the temporal relationships between WC and electrical current for the different testing conditions are shown, that the highest reduction in measured currents also occurred in the first and second weeks in that order.

Since high currents produce high electrical gradients, it is considered that this inevitably created greater physical (e.g. consolidation) and chemical (e.g. pH) changes. From Figure 6.3, with physiochemical changes occurring faster, the current had to keep dropping. The effect on rate of WC drop, therefore, had to be more in this period.

For all the anode-irrigated investigations, the average WC values from the second week (or there about) were more stable (refer to Figure 6.4). That is from around that period, the WC for any particular irrigated specimen, at all its respective positions was either constant or reducing at a much smaller rate. Additionally, during this same time, the observed shrinking and cracking (evidence of consolidation process) had stopped. The soil specimen was firmer and did not have the 'soup – like' consistency any more. It is assumed that the soil was by now 'reasonably' densified. Once the soil was in this denser state, it is thought that the suction (created by the insufficient supply of water) had minimal or / no more effect on the orientation of soil particles. This force was therefore likely to be mainly transferred to dragging the pore moisture and any film of fluid adsorbed on the clay particle surfaces in the direction of the cathode electrode. This should have facilitated the movement of the charged particles, which in turn would facilitate steady state power conditions. It is noted that the electrical current was being consumed steadily during this stage of the experiments (refer to Figures 6.1 and 6.4). With the steady state current comes the steady state WC. Figure 6.5 below illustrates this simplistic hypothesis of the steady state conditions experienced in the second phase during experimentation.

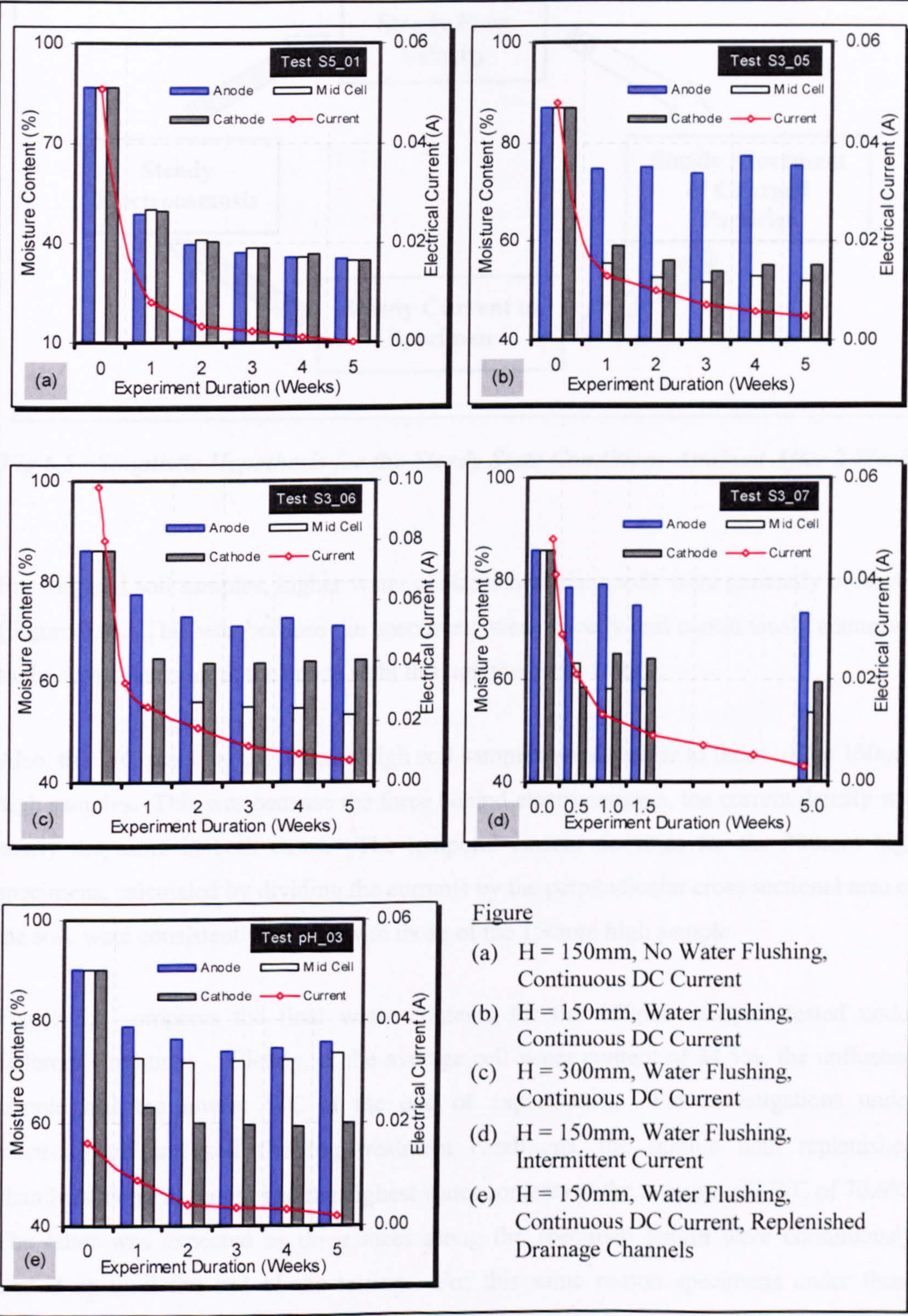


Fig 6.4 Temporal Relationship between Average Positional WC and Electrical Current for the Different Testing Conditions

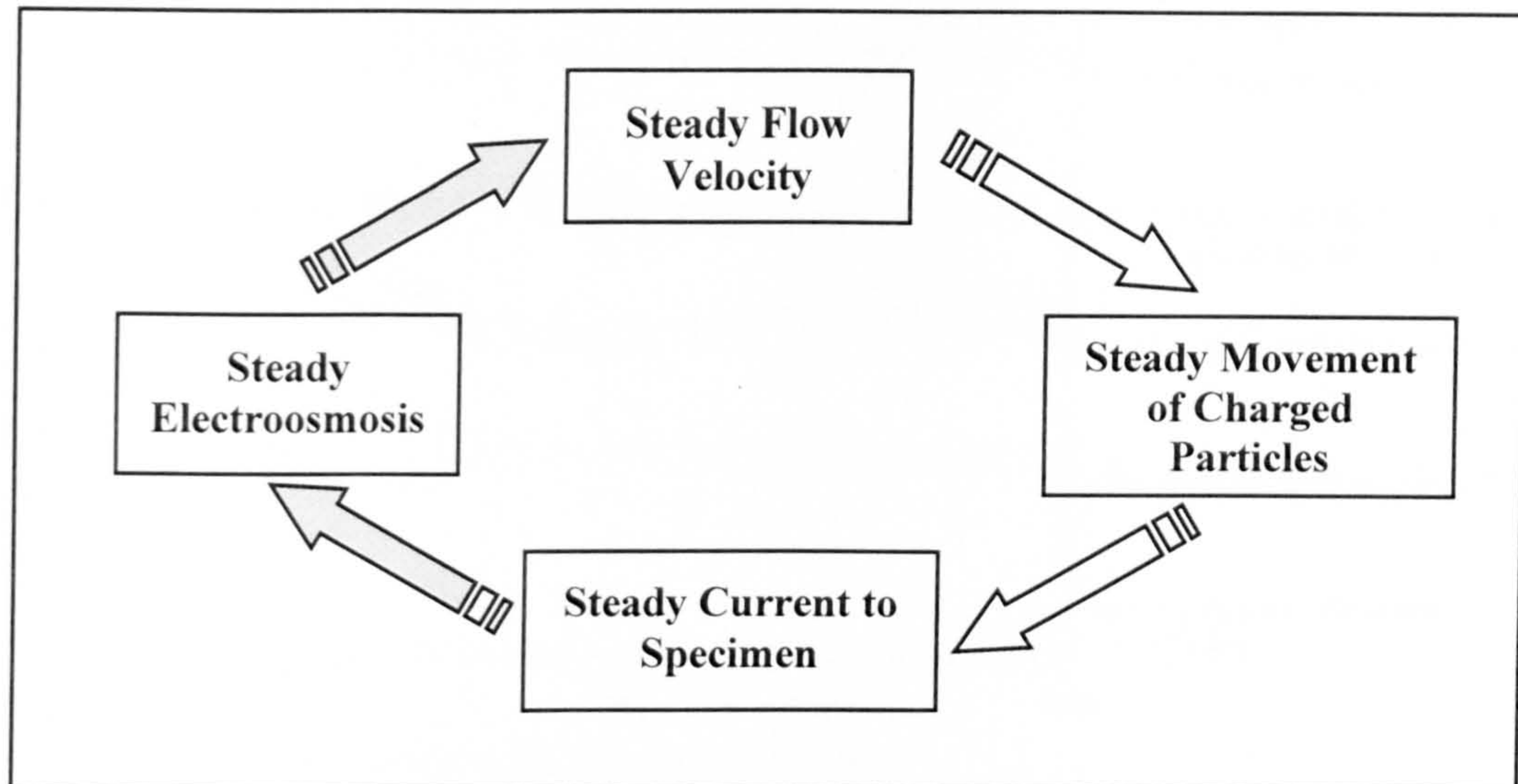


Fig 6.5 *Simplistic Hypothesis for the Steady State Conditions Attained After 2 Weeks*

For irrigated soil samples, higher water contents near the anode were generally observed (Figure 6.4). This was because the specimens were directly and continuously connected to the water reservoir at the anode right through the entire testing.

Also, the WC plots for the 300mm high soil samples were similar to those of the 150mm high samples. This was because the force behind electroosmosis, the current density was nearly the same in both cases. The temporal current densities for the 300mm high specimens, calculated by dividing the currents by the perpendicular cross sectional area of the soil, were consistently similar with those of the 150mm high sample.

Figure 6.6 compares the final water contents for the 150mm samples tested under different conditions. Clearly, at the average cell water content of 34.5%, the unflushed sample had the lowest WC at the end of experiments. For investigations under electrokinetic and soil flushing treatment conditions, the sample with replenished chambers along its length had the highest water contents at the average cell WC of 70.6%. The latter was expected as three faces along the specimen length were continuously wetted up until the end of the testing. For this same reason specimens under these conditions had the highest WC at any time during electrokinetic treatment.

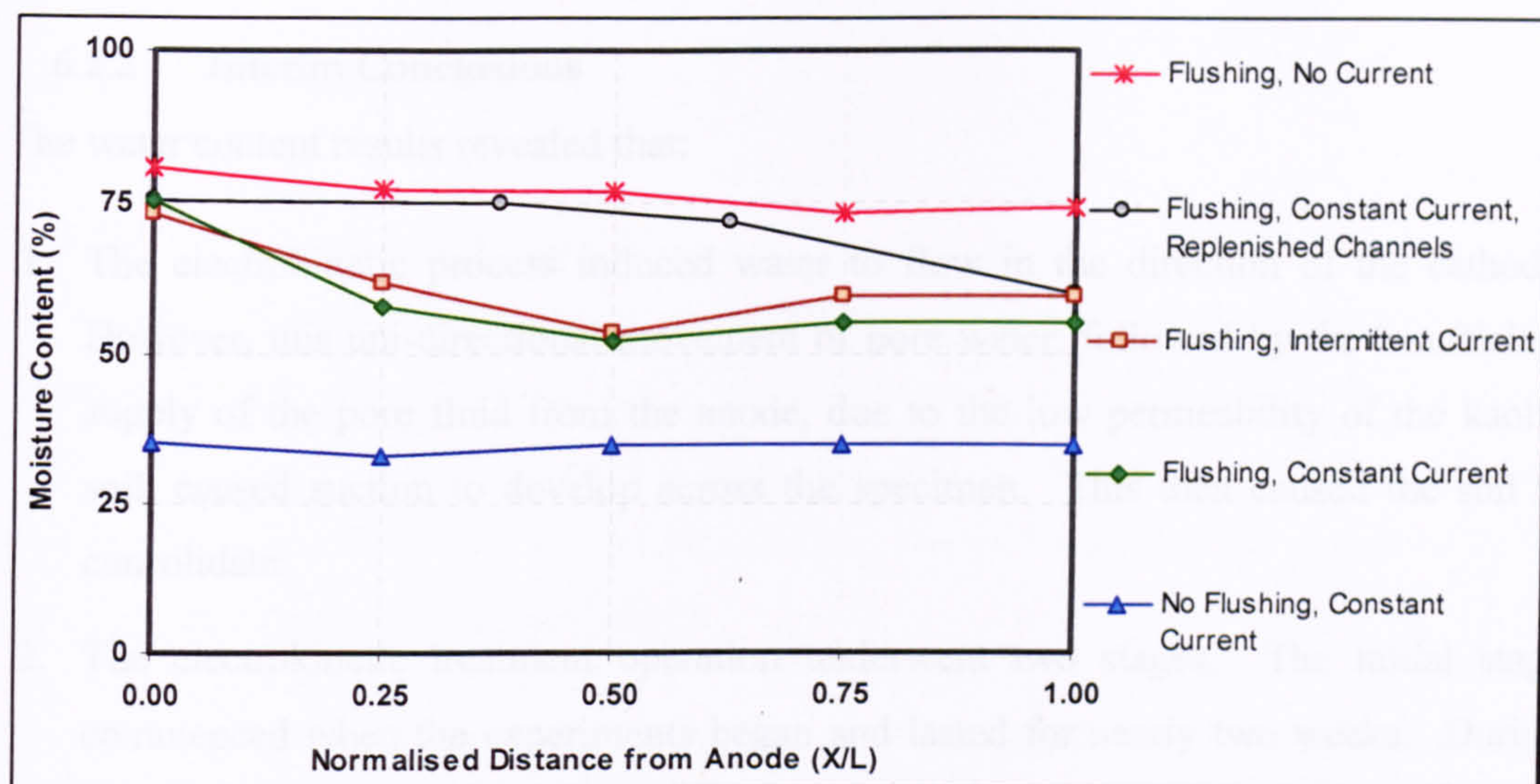


Fig 6.6 Ultimate WC along Cell for the Different Treatment Conditions

The test samples treated with the intermittent current also had final WC values slightly higher than the specimens with continuous direct current. It should also be highlighted that the WC values for experiments with intermittent current were for week ten. This is when that investigation ended (refer to Section 4.2.2.3 for the explanation). The evident slight differences in water contents were attributed to the variations in the electroosmotic flow that occurred as a result of the periodic changes in electrical gradient. The processes explained in the hypotheses above (Figure 6.3 and 6.5) definitely were occurring at a much slower rate as current was being periodically interrupted (24 hours on and 24 hours off).

Considering all the metal extraction options applied in this study, the control experiments - where water was allowed to seep across the test specimen without electrical enhancement - had the highest WC at any period during treatment. Since the soil material had a low permeability, only a very little amount of solution was able to seep out of the specimen as effluent. This is clearly demonstrated by the temporal variations of the effluent flow results presented in Figure 5.40. As a result, a high soil pore water presence was maintained throughout the five weeks testing programme.

6.2.2 Interim Conclusions

The water content results revealed that:

1. The electrokinetic process induced water to flow in the direction of the cathode. However, this uni-directional movement of pore water, followed by the insufficient supply of the pore fluid from the anode, due to the low permeability of the kaolin soil, caused suction to develop across the specimen. This then caused the soil to consolidate.
2. The electrokinetic treatment operation underwent two stages. The initial stage commenced when the experiments began and lasted for nearly two weeks. During this time, the contaminated specimens consolidated. In this same period, the current was at its highest but falling fast. The second stage of the experiment occurred after two weeks when the specimen had become stiffer and reasonably consolidated and the current was reducing steadily. During this period, the WC along the specimen was steadier with time. The observations could suggest that, during electrokinetic treatment, the degree of consolidation could have a major effect on the electro migration of the charged particles and ions. This in turn would affect the electroosmotic drive and consequently affect the WC content in the soil specimens.
3. The unflushed soil samples lost more water with time during electrokinetic treatment. During metal extraction, supplying deionised water constantly to the anode maintained higher water contents right through the specimen.
4. At any specific time during the clean up operation, the highest spatial water contents were experienced by the control experiments, followed by specimens with replenished drainage channels. Having waterlogged drainage channels along the soil profile increased the water content of the soil specimens during electrokinetic treatment. Operating soil-flushed-current free systems produced higher cell WC throughout the treatment programme due to the low permeability of the soil.
5. The spatial and temporal changes of WC in soil specimens with the same horizontal length and test conditions, but different heights were nearly the same although slight changes were evident. These slight changes could be attributed to minor variations in the electroosmotic flow and probably some procedural errors.

6.3 pH Distribution

6.3.1 Discussion of Results

To further understand the treatment characteristics of the water-flushed-constant-voltage treatment system, the pH distribution in the soil specimen was plotted in Figures 5.38 and 5.39. As pointed out in Section 4.2.2.4, the pH of unflushed test cases was not investigated since the pore water in the specimen was not sufficient to be trapped in the channels set up along the sample lengths.

The initial pH of the soil pore fluid was 5.4. It was observed that during five weeks of carrying out tests, the pH ranges of solutions at the anode and cathode were 2.3–2.5 and 9.5–10.5, respectively. These indicate that electrolysis reactions occurred at the electrodes. The pH values within the soil ranged from approximately 2.5 near the anode to 10.6 near the cathode. The pH variations were consistent with results reported by several investigators working with kaolin clay. In their studies, a distinct pH gradient was also created ranging from 2 near the anode to 12 near the cathode (Acar, et al. 1988; Acar and Alshawabkeh, 1993; Acar and Gale 1992; Hamed et al., 1991).

As discussed earlier in Chapter 2, the electrolysis of water results in the formation of H^+ ions (low pH) at the anode and OH^- ions (high pH) at the cathode, and, primarily due to electromigration, these ions tend to migrate towards the oppositely charged electrode(s). Since kaolin is a low acid buffering clay soil (Yeung et al. 1996, 1997; Puppala et al. 1997), the acidic solution generated at the anode typically migrated through the soil towards the cathode. By the end of the investigation, it had significantly lowered the pH through almost three quarters of the soil from the anode.

Conversely, it is also evident from these figures that an alkaline solution, generated by the electrolysis reaction at the cathode, migrated towards the anode and increased the pH in the soil region nearest to the cathode.

Analysing Figures 5.38 and 5.39, it can be seen for the first two weeks after starting treatment that more than half the specimen was basic. This is contrary to what had been expected for treatment under open anode conditions. Since:

1. there was initially a higher electroosmotic flow towards the cathode observed through the higher effluent flows in the first weeks as presented in Figure 5.40, (the direction of electroosmotic flows from the anode towards the cathode opposes the electromigration of OH^- ions towards the anode),
2. compared to H^+ ions, OH^- ions have larger ionic radii and a lower mobility and hence the H^+ ions usually migrate faster through the soil (Acar and Alshawabkeh, 1993). The transport of the H^+ ions is approximately two times faster than the OH^- ions (refer to Section 2.3.2.1), and
3. at higher voltage gradients higher current densities are generated which increase the rate of electrolysis reactions at the electrodes (there were higher currents initially),

The pH should have been much lower in the cell half on the cathode side in this period – prompting more than half the cell to be acidic. It had been thought that all the three points above should have benefited H^+ transport. Nonetheless, what was observed appeared to be a consequence of the high soil water content as in the first two weeks the specimen was wetter. The resulting soil particles during this time were more disperse. It is thought that this might have made it easier for the OH^- ions to migrate through the pore network towards the anode.

The plotted curves for the period from two weeks of testing onwards confirm that more than half the cell was and remained acidic. This is evident from Figure 6.7 which shows the pH along the soil profile for the fourth and fifth weeks. It can be established from this figure, that at the conclusion of the experiments, the neutral point ($\text{pH} = 7.0$) was in between the $\frac{1}{2}L$ and $\frac{3}{4}L$ positions. It is obvious that nearly three quarters of the cell was acidic. The two possible explanations for this observation are that:

- (a) the specimen water content had reduced to lower values (56% at the cathode) by this time, the specimen was fairly stiff (especially in the cathode half), and the soil had become denser due to consolidation. Laboratory observations showed that the closer the distance to the cathode the stiffer the soil got.

Research conducted by Hill (2004) at Nottingham University, showed rapid decline in leached ionic species over time with compacted soil material but general increase in trend of species in uncompacted material. The study concluded that the effect of

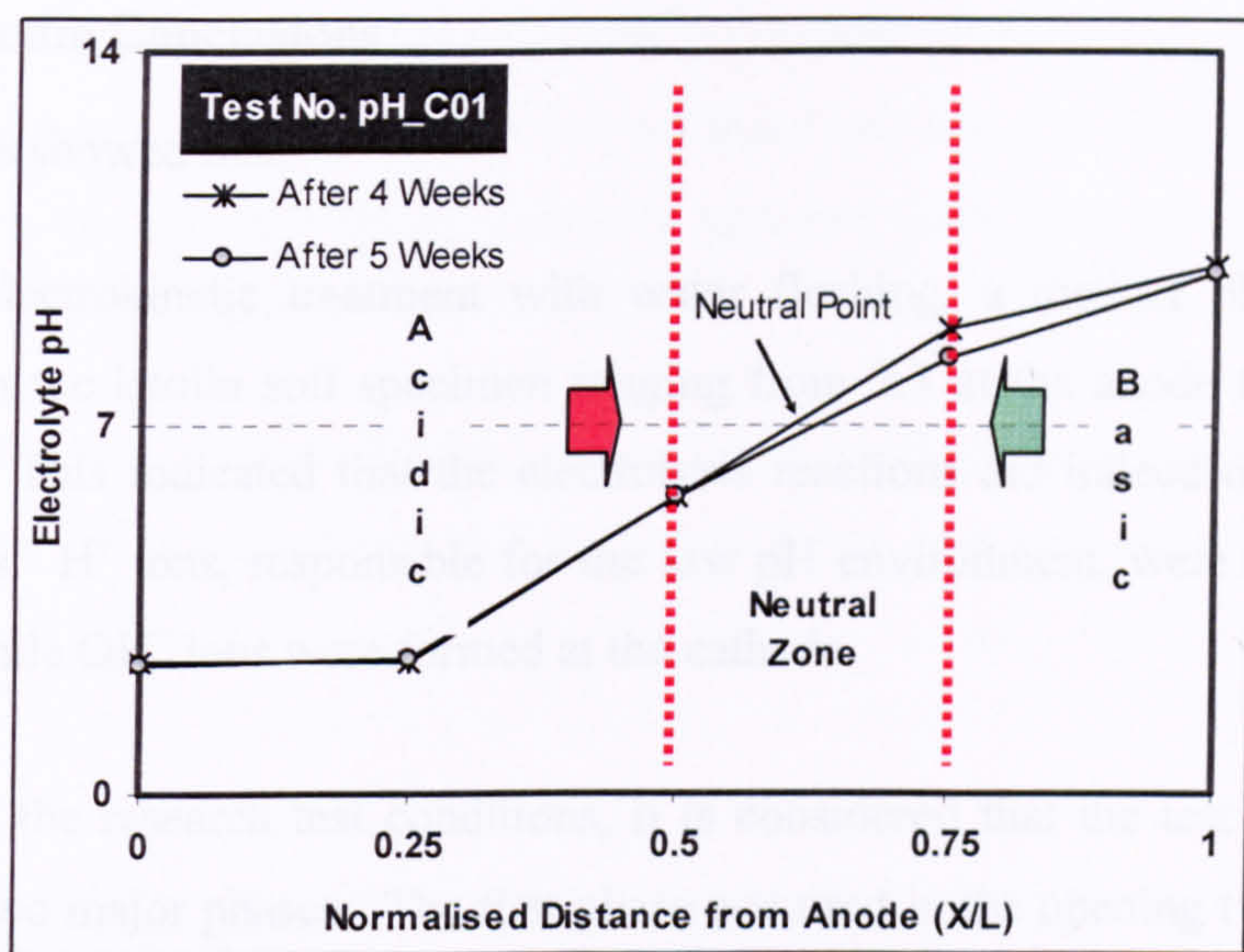


Fig 6.7 Variation of Electrolyte pH along Cell at End of Testing

density was most pronounced for materials with high fines content. Thus, it is possible that consolidation causes the fines to clog the pore spaces, diminishing the flow paths which then impede the movement of ions.

Accordingly, it is thought that when the soil was denser, it was difficult for the larger and less mobile OH^- ions to penetrate into the soil from the cathode. Lower WC and higher compactness of the soil could have favoured the mobility of the smaller H^+ ions. This occurrence of low mobility of OH^- ions (than H^+ ions) was also observed by Reddy et al. (2002) for tests conducted on kaolin at low, 30%, water contents.

- (b) There was continuous reduction of OH^- ions due to chemical reactions in the soil close to the cathode. It is possible that Zn arriving at the cathode side tended to combine with OH^- to produce Zinc Hydroxide ($\text{Zn}(\text{OH})_2$) - (the highest concentration of Zn was measured at the cathode compartment at this phase of treatment). And if indeed most of the generated OH^- ions at the cathode compartment were consumed by the Zn in generation of $\text{Zn}(\text{OH})_2$, as a result, the high pH in soil near the cathode zone would not be able to advance further.

Figure 6.7 also gives an understanding of the pH compartmentalisation of the cell at the closing stages of the investigation. The region between the anode and $\frac{1}{2}L$ was the most acidic and characterised by the lowest pH while that between the cathode and $\frac{3}{4}L$ was basic. The section between $\frac{1}{2}L$ and $\frac{3}{4}L$ was considered to be a neutral zone. This is where the two fronts i.e. the H^+ and OH^- merged.

6.3.2 Interim Conclusions

The pH results showed that:

1. During electrokinetic treatment with water flushing, a distinct pH gradient was created in the kaolin soil specimen ranging from 2.3 at the anode to 10.6 near the cathode. This indicated that the electrolysis reactions did indeed occur at the two electrodes. H^+ ions, responsible for the low pH environment, were produced at the anode, while OH^- ions were formed at the cathode.
2. Based on the research test conditions, it is considered that the test processes went through two major phases. The first phase occurred in the opening two weeks when the test specimen was partially saturated and less dense. At that time the base front advanced towards the anode faster than the acid front. The second phase occurred after the second week when the advancement of the acidic front in the opposite direction was faster. At that moment, the water content was lower than that at the start. The WC in the soil specimen was steadier (reduction rate was at its minimum), the current reduction was stable and the sample was fairly stiff and dense especially at the cathode area.
3. The WC and specimen density do have an effect on the pH during electrokinetic treatment, but the effect could probably be most appreciated at the region nearest to the cathode where the OH^- ions are generated.

6.4 Metal Migration and Removal

6.4.1 Zinc Extraction Discussion

Figure 6.8 illustrates the normalised contaminant concentrations that were measured along the soil profile after the electrokinetic and soil flushing processes were completed for the tests conducted under different experimental conditions. The results were normalised in order to provide comparison of results between experiments. The concentration of Zn ions present in localised position of the sample was normalised by dividing the measured average positional concentration by the total concentration of the metal ions in the soil prior to treatment. Generally, all the concentration profiles of electrokinetics remediation show an increase in metal concentration with increase in

distance from the anode. This indicates that cation transport did indeed occur from the anode towards the cathode. This is further evidence that once the electrokinetics process was underway, the Zn ions being positively charged were attracted to the negatively charged electrode (cathode).

However, by the end of electrokinetic treatment, the trends in metal concentrations along the profile were divergent between soil specimens which had been purged with water and those that were not.

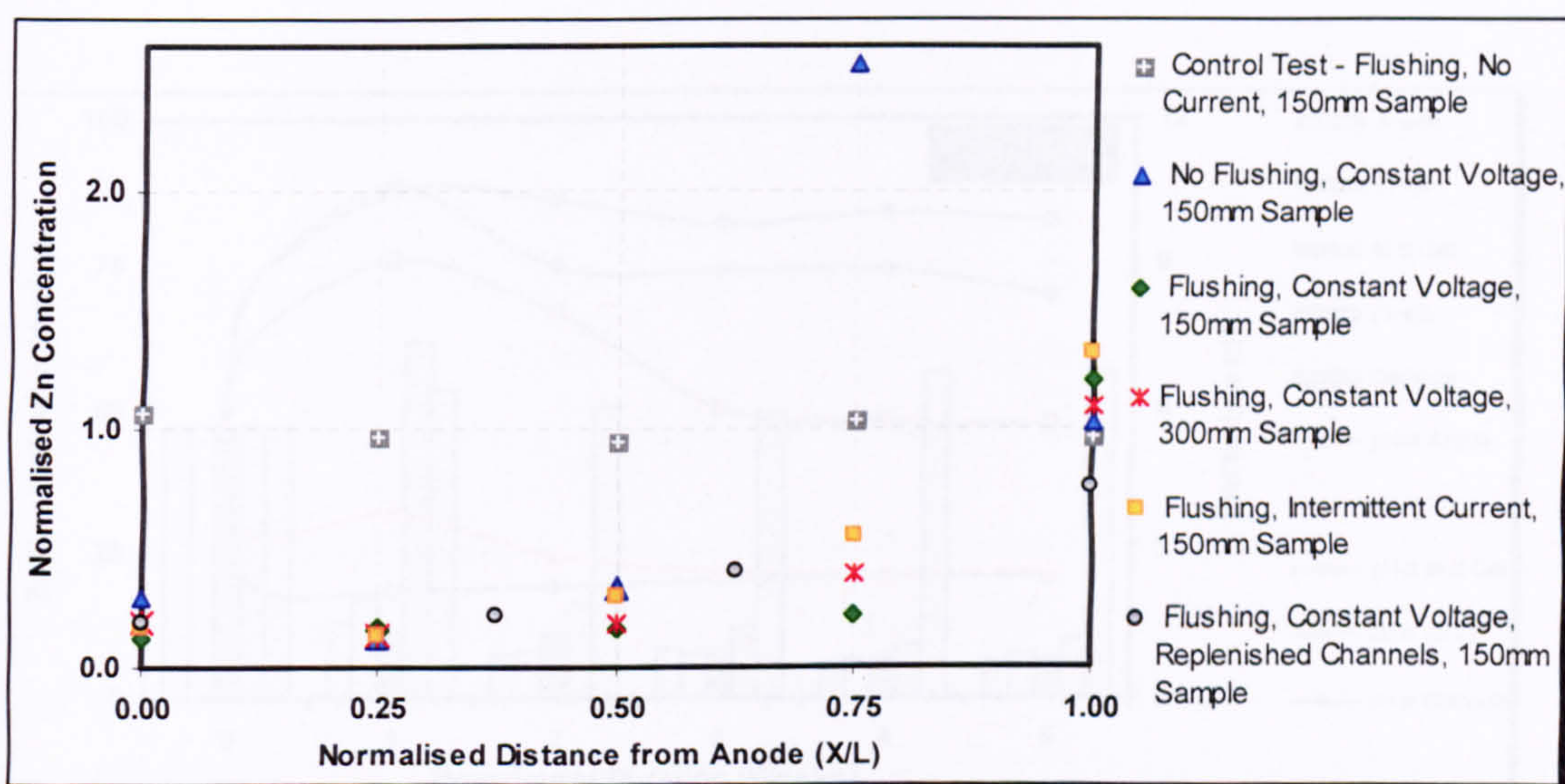


Fig 6.8 Post Treatment Zinc Distribution for the Different Test Conditions

For the flushed specimen cases, it was observed that the metal concentration decreased by about 75% in the three quarters of soil length from the anode. In all these cases, the cation accumulation was always in the direction towards the cathode. At the region between the anode and $\frac{1}{4}L$, the metal concentration at the end of the investigation was nearly the same.

In Figure 6.9, the temporal relationships between the average positional Zn concentration and cell electrolyte pH for the 150mm open anode constant voltage supplied soil samples are shown. It is evident that the low pH in the anode half of the cell was being matched by low metal concentrations in that section. According to Acar et al. (1989), reduced pH is beneficial in desorption of metals from soil surfaces, as well as preventing metals from

precipitating out of solution. This implies that under the acid environment in the anode half of the cell, the contaminant was sustained in solution. As a result of the applied potential gradient, the cations were able to progressively migrate by electroosmotic and electromigration forces towards the cathode. The identical pH values at the anode and $\frac{1}{4}L$, achieved from the third week, explains why similar Zn concentrations were observed at these positions by the end of the tests.

At the cathode and its vicinity, where the pH was clearly high, metal accumulation was observed from the end of the first week of operation. At the $\frac{3}{4}L$ position, though, the Zn

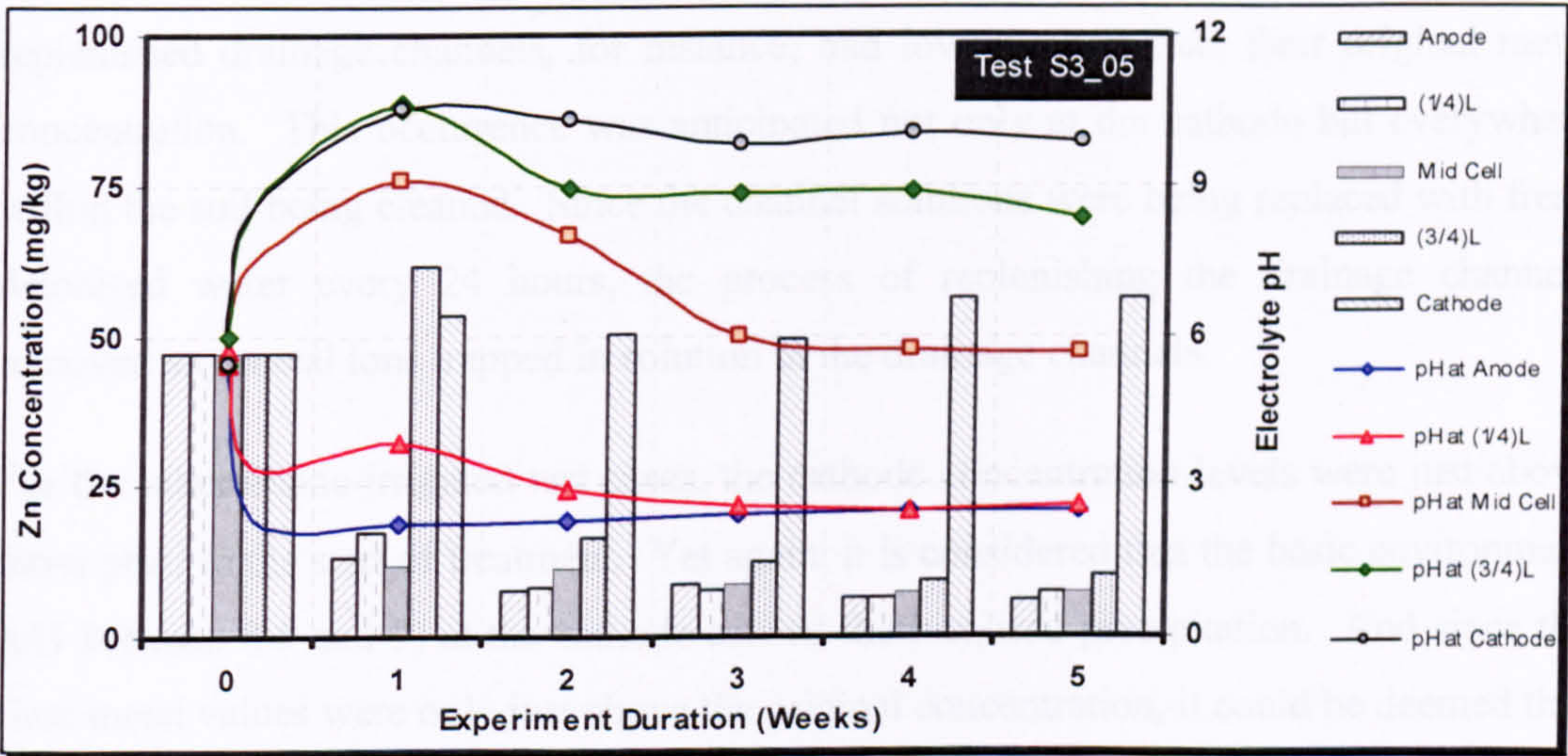


Fig 6.9 Temporal Relationship between Average Zn Concentration and Electrolyte pH for the 150mm Open Anode Cell

concentration started to decrease from the second week onwards as the pH was gradually dropping there. At the cathode compartment where it remained as high as 10, a high metal presence was maintained until the end of treatment (Figure 6.9). Due to the basic environment at this end of the cell, the metal cations unable to reach the effluent chamber with the purge water precipitated out of solution resulting in a comparatively high contaminant concentration.

Thus, the presence of low pH in the majority of the soil at the end of the electrokinetics-soil flushed experiments (Figure 6.9) did indeed lead to better metal extractions in three quarters of that cell. This, therefore, part explains why all test specimens with open anode

conditions experienced metal reductions in three quarters of the soil mass - as shown in Figure 6.8.

In Figure 6.10 the temporal relationship between average positional Zn concentration and electrical current for the different testing conditions is presented. It is clear from the graphical plot that the highest fall in current for all test cases occurred during the initial two weeks when the most notable metal cation migration was observed. In the final stages of all these experiments, the current was at its lowest but still reducing. Lower currents in later phase of treatment were, thus, less enabling for ionic species movement.

It is also shown in Figure 6.8 that there were variable ultimate metal ions concentrations at the cathodes of the different water flushed experiments. The specimens with replenished drainage channels, for instance, had lower values than their original metal concentration. This occurrence was anticipated not only at the cathode but everywhere within the soil being cleaned. Since the channel solutions were being replaced with fresh deionised water every 24 hours, the process of replenishing the drainage channels removed any metal ions trapped in solution in the drainage channels.

For the other anode-irrigated test cases, the cathode concentration levels were just above those prior to the start of treatment. Yet again, it is considered that the basic environment (pH between 8.5 and 9) at the cathode caused the localised precipitation. And since the final metal values were only just above the original concentration, it could be deemed that most of the metals which migrated from the rest of the soil to this electrode end, filtered into the effluent chamber with the rest of the purge solution. This was further evidence that the effect of electroosmosis was strong to prop up migration of the cation to the cathode, through the filter layer, into the effluent chamber. In fact, from the analysis of the effluent results, in Figure 5.42, it is apparent that more Zn was removed by the combined effort of electrokinetic and soil flushing than with soil flushing only.

It is also thought that, besides precipitation mentioned in the earlier paragraph, the consolidation of the soil around the cathode area could have impeded the local mobility of the metal ions in this later stage of experimentation – the effect of change of density on movement of ions has been discussed in Sections 6.2.1 and 6.3.1. The results could suggest that there is a certain density threshold for the efficient electromigration of metal ions beyond which, their movement is restricted.

For the two different specimen depths (i.e. 150mm and 300mm) conducted at constant voltage with open anodes, an almost identical final metal removal was experienced at all positions except $\frac{3}{4}L$. Within the experimental margin of error, it can be concluded that doubling the specimen height did not significantly affect the ultimate migration of the metals ions. This was possibly expected because, though the height had been doubled, the current density (which is a function of current and cross sectional area) essentially remained the same. This is supported by Reddy and Chinthamreddy (2004) whose study concluded that the amount of ion electromigration occurring was a characteristic of the current density.

Although intermittent current saved on the energy consumption during the intervals it was off, the outcome showed that no treatment improvement was achieved by this method. The contaminant concentration values were about the same in the anode half of the cell with those of the specimen treated at constant voltage supply. Further analysis of the results showed that the samples with intermittent current registered lower contaminant extraction from $\frac{1}{2}L$ right through to the cathode. In fact, this was even achieved at practically twice the time the specimen treated with uninterrupted current took. This implied that to achieve similar results would require just over double the duration. Consequently, the sequence of events anticipated in Section 4.2.2.3 may not have taken place as expected. During the intervals when the current was off, it is now considered that no metal transportation occurred. And the momentum of the previously moving Zn ions stopped. So when the power was switched on 24 hours later, it could have taken a few seconds before building this momentum again. These on and off cycles therefore could have resulted in the overall slower mobility of the Zn ions, hence the lower species removal experienced especially in the cathode half. Perhaps faster switching needed to be attempted as per Mohamedelhassan and Shang (2001).

For the unflushed test samples, the decrease in ultimate cation concentration was only registered in one half of the cell - the anode side. However, there was considerable increase in the metal species in the other half from the cathode. The amount at $\frac{3}{4}L$ was more than two and a half times the original value. This was the highest metal concentration any where in the soil. The accumulation of Zn at $\frac{3}{4}L$ was basically a function of high pH encountered at that location and subsequent formation of precipitation products of Zn. Because flushing water was not added at the anode during the electrokinetic processing, the amount of electroosmotic volume flowing from the

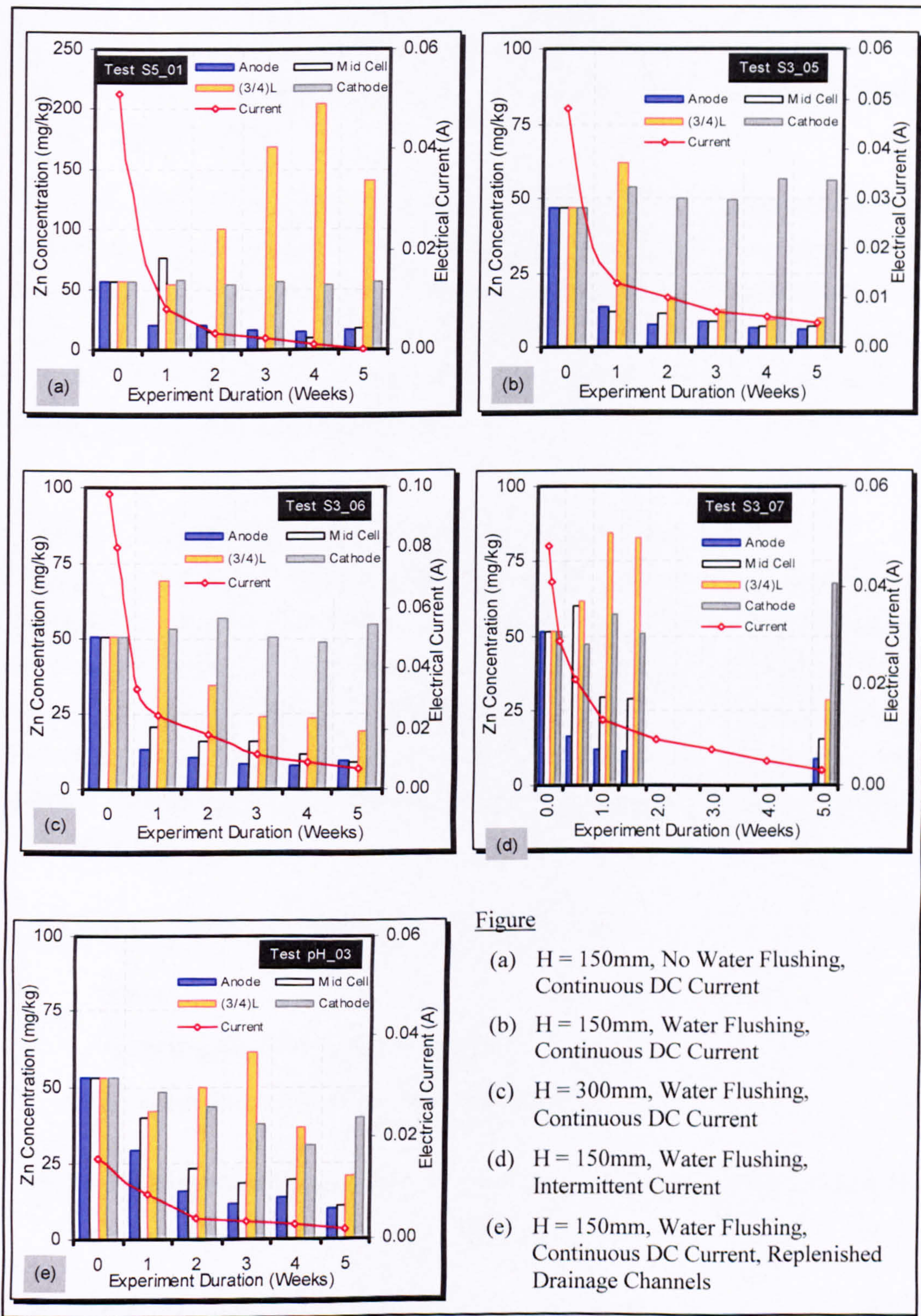


Fig 6.10 Temporal Relationship between Average Positional Zinc Concentration and Electrical Current for the Different Testing Conditions

anode towards the cathode was insufficient to oppose the electromigration of OH^- ions towards the anode. This, then, resulted in the high pH which caused the metal ions to come out of solution. With the metal species out of the liquid phase in the soil pores, they could no longer be electro transported to the cathode. The effect of no-flushing is, therefore clearly evident.

Of all the different investigations conducted, only the control experiments showed no notable changes in Zn concentration along the entire cell length. The water flushing, across the control test cell under the hydraulic gradient, was not sufficient to 'wash' significant amounts of the cations into the effluent chamber without any enhancement. For the period of 5 weeks treatment, only 693 ml of effluent was collected compared to 8300ml from the electrokinetic treatment.

6.4.2 Extraction Efficiency and Electrical Energy Consumed

Weekly average cell Zn concentrations for the different investigation situations were calculated and tabulated in Table 6.2. The average values were calculated by summing up the respective weekly contaminant concentrations along the cell, and dividing by the total number of sampling positions. Weekly Zn Removal Efficiency, Overall Removal Efficiency, Weekly Electrical Energy Consumed and Total Energy Consumed per cubic meter of Treated Soil, were also computed using the equations below and then presented in the same table.

$$(a) \text{ Weekly Zn Removal Efficiency (\%)} = 100 \times (X_n - X_{n-1}) / X_i \quad - \quad 6.2$$

Where:

X_n - Average Zn Concentration in Week n ($1 \leq n \leq 5$)

X_i - Initial Zn Concentration of the Soil Specimen

$$(b) \text{ Overall Removal Efficiency (\%)} = \text{Summation of the 5 Weekly Zn Removal Efficiencies} \quad - \quad 6.3$$

$$(c) \text{ Weekly Electrical Energy Consumed , E} = I \times V \times T \quad - \quad 6.4$$

Where:

E - Electrical Energy (in Kilo Watt Hour)

I - Electrical Current (in Amps)

V - Voltage (in Volts)

T - Experiment Duration (in Hours)

$$(d) \text{ Total Energy Consumed per m}^3 \text{ per of Contaminated Soil} = E \div Vol \quad - 6.5$$

Where:

Vol - Volume of the Contaminated Soil Treated (in m³)

The results of the weekly contaminant removal efficiency and electrical energy consumed are also plotted in Figures 6.11 to 6.13

It is evident in Table 6.2 and Figures 6.11 to 6.13 that:

- 1) All metal extraction processes (with the exception of the One Process Approach experiments which were run with electrokinetics process only) showed general decline in average weekly cell metal concentrations with time. The observations in the One Process, showed reductions in average weekly concentration but only up to the third week. Because the contaminant ions leached from the cells with the effluent during treatment, the overall cell metal concentration was expected to decrease with time. The anomaly in the One Process results could therefore have been due to procedural errors and/or the inaccuracy of using the averaging method in estimating the average cell contaminant concentration.
- 2) The highest weekly metal extraction efficiencies were in the initial two weeks of clean up with the weekly efficiencies dropping with time. During the first two weeks of electrokinetic treatment, nearly 90% of the electrical energy had been consumed in the remediation process.
- 3) The specimens with replenished drainage chambers had the highest overall metal removal efficiency to energy consumed per cubic meter of contaminated soil treated ratio, followed by cells with intermittent currents.

Table 6.2 Relationship between Zinc Extraction Efficiency and Energy Consumed

Experiment		Treatment Period	Average Weekly Zn Concentration During Treatment	Weekly ^(a) Zn Removal Efficiency	Overall ^(b) Removal Efficiency	Weekly ^(c) Electrical Energy Consumed	Total Energy Consumed ^(d) per m ³ of Treated Soil
		(Weeks)	(mg/kg)	(%)	(%)	(kWh) - [%]	(kWh/m ³)
Control (Soil Flushing only)		0	49.09	-	0.3	N/A	N/A
		5	48.90	0.3		N/A	
One Process Approach (Electrokinetics only)		0	55.49	-	14.6	-	12.52
		1	45.14	18.6		0.130 [84.2]	
		2	42.21	5.3		0.014 [9.2]	
		3	53.98	-21.2		0.004 [2.3]	
		4	58.72	-8.5		0.004 [2.3]	
		5	47.39	20.4		0.003 [2.0]	
Two Stage Approach (Electrokinetic and Soil Flushing)	Sample Height 150mm with Continuous Current	0	46.85	-	63.2	-	10.57
		1	31.60	32.6		0.106 [81.4]	
		2	18.83	27.3		0.009 [7.0]	
		3	17.36	3.2		0.009 [7.0]	
		4	17.10	0.5		0.003 [2.3]	
		5	17.24	-0.3		0.003 [2.3]	
	Sample Height 300mm with Continuous Current	0	50.08	-	60.4	-	11.18
		1	35.11	29.9		0.222 [80.8]	
		2	25.91	18.4		0.020 [7.1]	
		3	21.66	8.5		0.018 [6.6]	
		4	19.50	4.3		0.009 [3.3]	
		5	19.84	-0.7		0.006 [2.2]	
	Sample Height 150mm with Intermittent Current	0	51.50	-	51.2	-	5.53
		0.5	43.84	14.9		0.041 [58.7]	
		1	39.10	9.2		0.012 [17.4]	
		1.5	36.62	4.8		0.005 [6.5]	
		5	25.12	3.2		0.002 [2.2]	
	Sample Height 150mm with Continuous Current and Replenished Drainage Channels	0	53.14	-	61.5	-	3.73
		1	39.69	25.3		0.021 [50.0]	
		2	33.01	12.6		0.015 [35.7]	
		3	32.14	1.6		0.002 [3.6]	
		4	25.16	13.1		0.002 [3.6]	
		5	20.46	8.9		0.003 [7.1]	

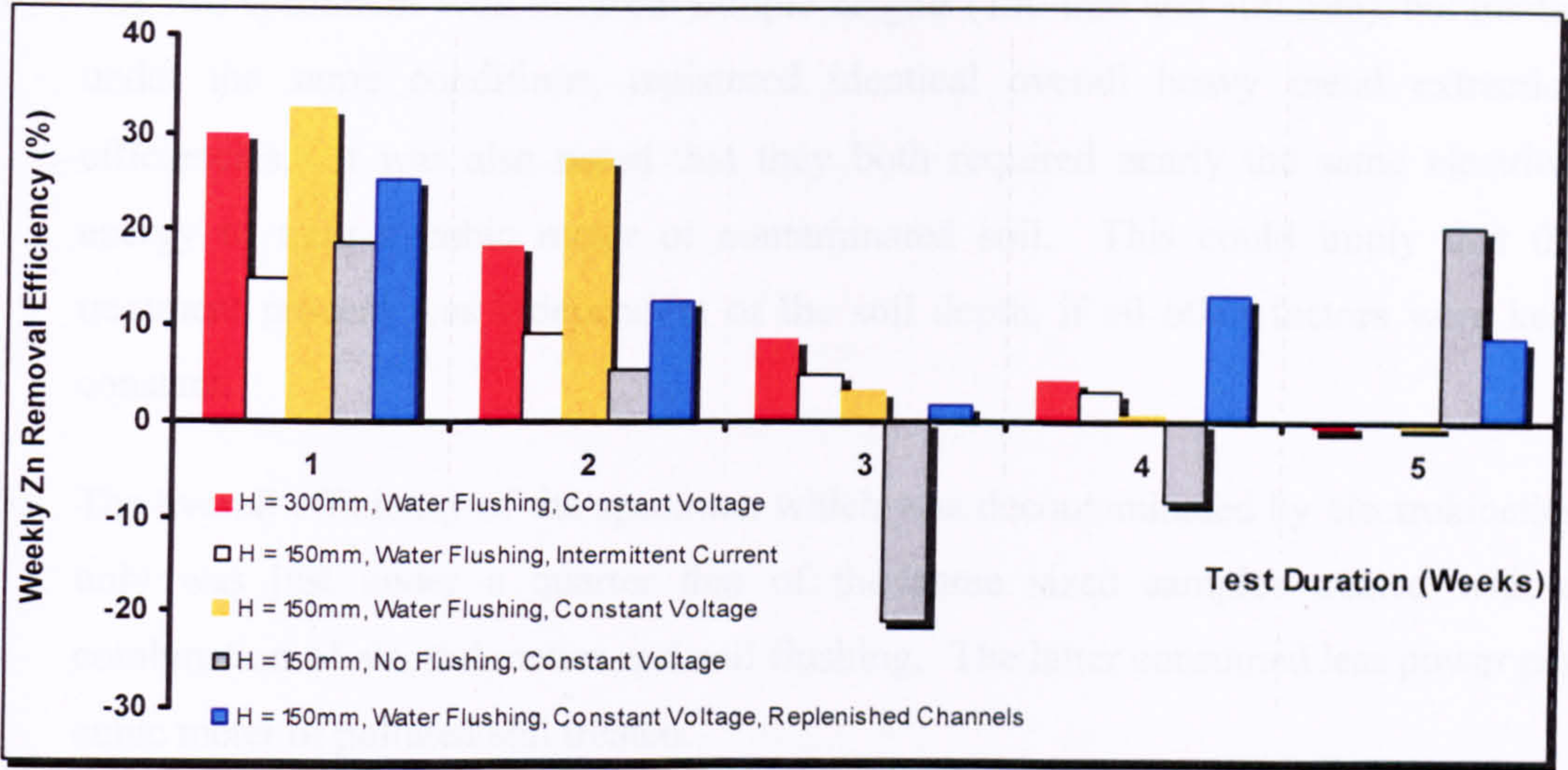


Fig 6.11 Weekly Percentage Zinc Extraction Efficiency

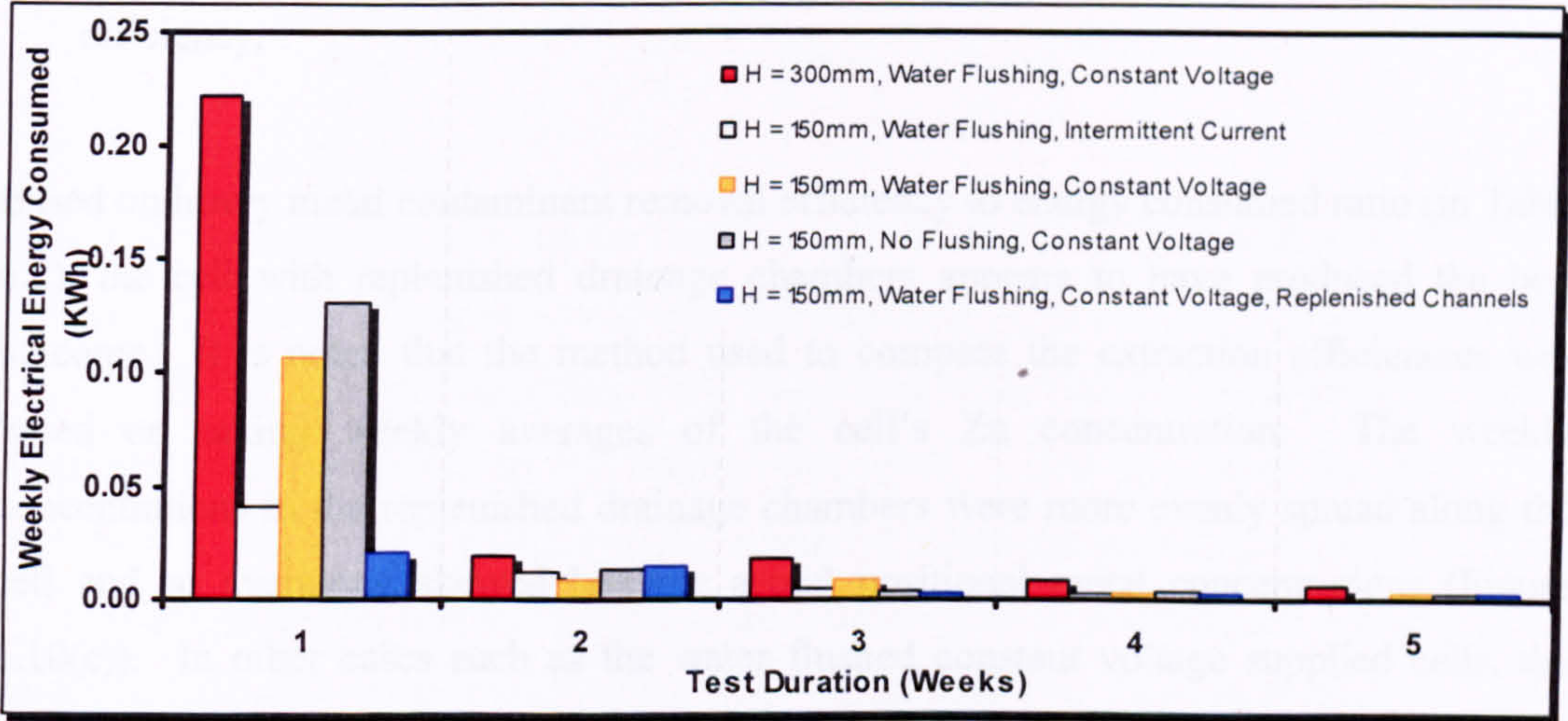


Fig 6.12 Weekly Electrical Energy Consumed

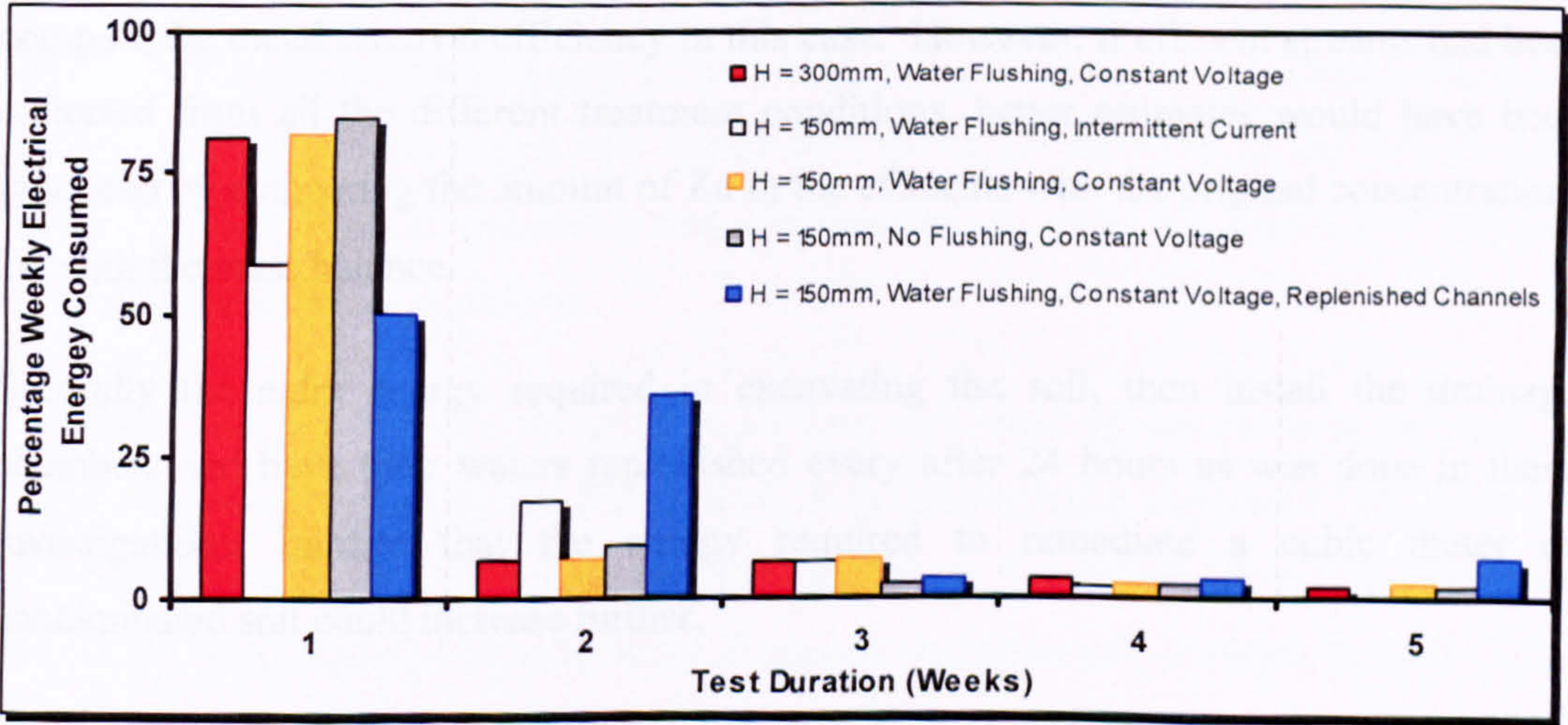


Fig 6.13 Percentage Weekly Electrical Energy Consumed

- 4) The two specimens with different sample heights (150 mm and 300 mm), but treated under the same conditions, registered identical overall heavy metal extraction efficiencies. It was also noted that they both required nearly the same electrical energy to treat a cubic meter of contaminated soil. This could imply that the treatment process was independent of the soil depth, if all other factors were kept constant.
- 5) The overall efficiency of the specimen which was decontaminated by electrokinetics only was just under a quarter that of the same sized samples treated with a combination of electrokinetics and soil flushing. The latter consumed less power per cubic meter of polluted soil treated.
- 6) As expected, the control experiments recorded the lowest overall metal extraction efficiency.

Based on heavy metal contaminant removal efficiency to energy consumed ratio (in Table 6.2), the cell with replenished drainage chambers appears to have produced the best outcome. It is noted that the method used to compute the extraction efficiencies was based on taking weekly averages of the cell's Zn concentration. The weekly concentrations in the replenished drainage chambers were more evenly spread along the cell and so averaging skewed less the actual positional metal concentrations (Figure 6.10(e)). In other cases such as the water flushed constant voltage supplied cells, the metal ions were concentrated at the cathode end with minimal levels elsewhere in the soil mass (Figure 6.10(b)). Thus, averaging was probably not the most suitable method to compute the metal removal efficiency in this case. However, if effluent streams had been collected from all the different treatment conditions, better estimates would have been produced by comparing the amount of Zn in the effluents with the original concentrations i.e. with the mass balance.

Secondly the extra energy required in excavating the soil, then install the drainage chambers and have their waters replenished every after 24 hours as was done in these investigations, implies that the energy required to remediate a cubic meter of contaminated soil could increase further.

The intermittent cells which also attained good metal removal efficiency to energy consumed ratio had a lower overall extraction efficiency than the 150mm high cell remediated with both electrokinetics and water flushing. Besides, the former was conducted at practically twice the duration of the latter.

Overall, basing on results of Table 6.2 and the discussion above, the 150mm and 300mm high cells remediation conditions were the most recommendable for application in soil decontamination. In both test scenarios - treatment was by combination of electrokinetics (with continuous direct currents) and soil flushing - the heavy metal species were concentrated at cathode electrode region by the time testing ended. This implies that at the ultimate stage, the pollutants were confined to a small area. To complete treatment and achieve even better extraction targets, the soil material in cathode section could easily be dug up and taken for disposal.

6.4.3 Mass Balance

After the electrokinetic tests for the One Process and the Two Process Approaches were completed, a mass balance was conducted for the Zn in the system: i.e. soil in the test cell, effluent discharges, anode irrigating water remaining in the flushing chamber at the end of processing, and compared to the original Zn spike. The details of the results are presented in Tables A5.4 to A5.8 in the appendix, while the summary is given in Table 6.3 where it is shown that there were notable differences in contaminant recovery (total amount of Zn after / before test) by the One Process and Two Process treatments. In the former (i.e. contaminated soil treated without flushing with deionised water), the recovery in the effluent appeared to be 6.7% compared to 11.3% for the experiment where the effect of electrokinetics was coupled with soil flushing. The recovery difference between the two tests was 4.6% which was nearly two thirds the recovery in the One Process treatment. The result demonstrates that soil flushing enhanced the removal of the zinc metal cations from soil specimen.

The mass balances of zinc in the One Process and Two Process tests at the end of processing are also presented in Figure 6.14. It is demonstrated that about 71% and 97% of the original total zinc remained in the soil sample. Differences in the results of the two tests were attributed to the differences in sample water contents during treatment. The

Table 6.3 Mass Balance for the One Process and Two Process Cells after 5 Weeks of Electrokinetic Treatment

Section	<u>One Process Cell</u>		<u>Two Process Cell</u>	
	Initial Conc. = 45.12 mg/kg Soil Slurry in Cell = 13.07 kg WC = 85.42 % Total Zinc in Cell = 271.67 g		Initial Conc. = 42.67 mg/kg Soil Slurry in Cell = 12.88 kg WC = 85.52 % Total Zinc in Cell = 253.34 g	
	Zinc (mg)	% of Original Zinc Spike	Zinc (mg)	% of Original Zinc Spike
Treated Soil	264.9	97.5	181.46	71.6
Effluent	18.26	6.7	28.57	11.3
Water in Flushing Chamber			0.16	0.1
Total	283.1	104.2	210.20	83.0
Error		4.2		-17.0

diminishing water content in the treated samples stalled the movement of the contaminants, thereby resulting in higher residual concentration of Zn in the unflushed specimen.

In this investigation, the One Process test had a zinc mass error that was computed to be within 4% of the initial zinc mass, while that of the Two Process test was within 17%. Discrepancies in the mass balance were largely attributed to uneven contaminant distribution within the soil system. The method of determining zinc along the profile of the treated soil mass, assumed that the concentration of the collected samples (determined using the AAS) was the same as that of the soil within in the vicinity of the sampled position. In most tests, each sample collected for testing represented about half a

kilogram of soil in the test cell. Because of the non homogeneity of for example the electric field distributions (Section 3.2.3), variations in the concentration at any reference position were likely and therefore could affect the results.

The other sources of error may have been detection limitations in the chemical analyses, or contaminant adsorption to the electrokinetic equipment, such as the perspex chambers, the electrodes, filter system, tubing, and/or sample bottles. The error could also have been related human, instrumental, and/or other procedural errors.

In both tests, though, the mass balance error was less than 20%. This error was not expected to significantly affect the quality of data collected. In any case, an error of less than 20% in mass balance calculations was within the target limit of other researchers such as Acar et al. (1997) whose quality control project plan objective was a maximum mass balance error of 20%. The procedure used to determine this value was however not given by Acar and his research team.

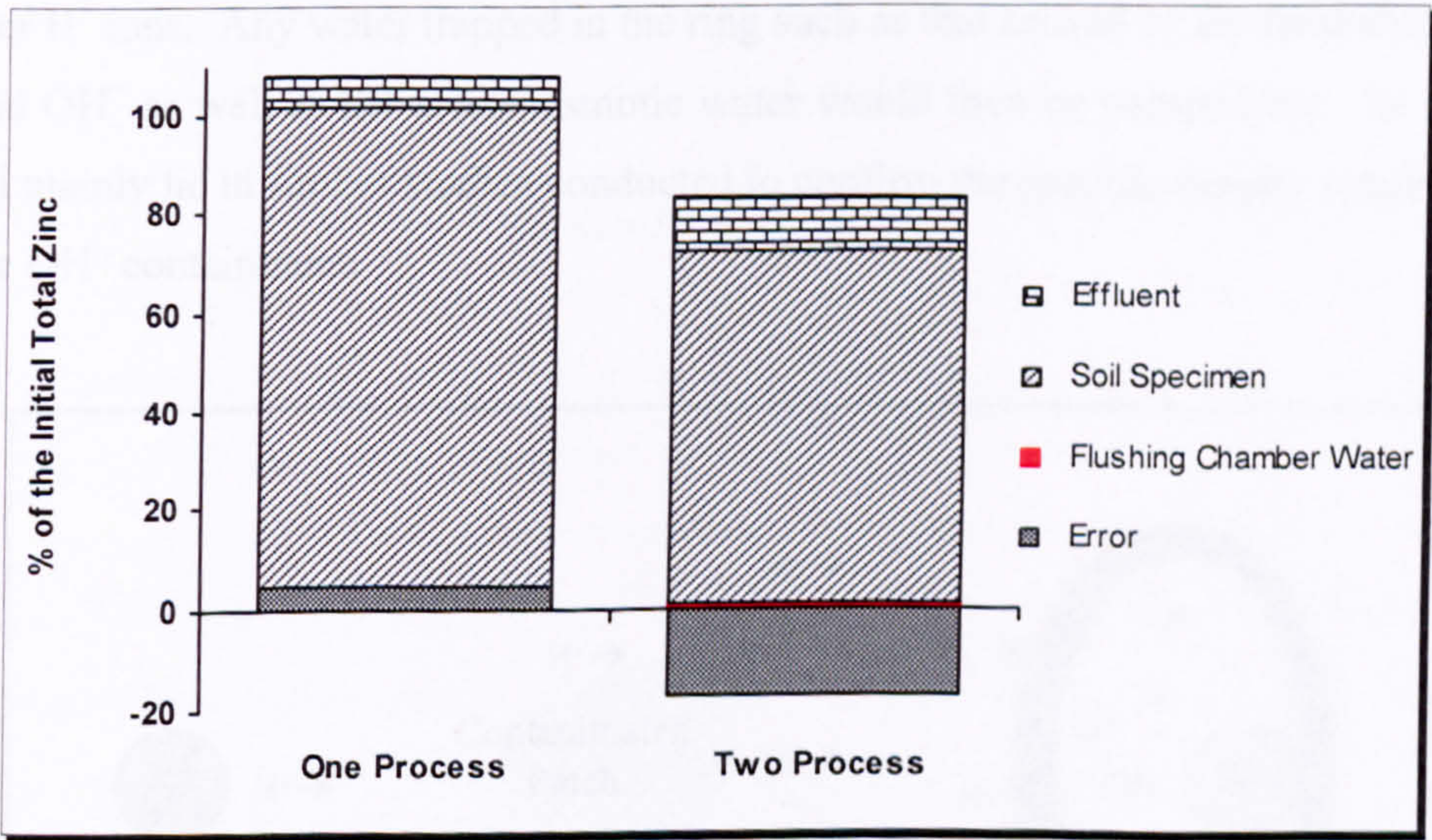


Fig 6.14 Mass Balance for the One Process and Two Process Cells after 5 Weeks of Electrokinetic Treatment

6.4.4 Modified Model for Efficient Performance

Acar and Gale (1992) - whose pH results were consistent with those of this study - showed that the efficiency of the process for heavy metal removal depended on the extent to which the acid front reached the cathode. However, the results of this study of the specimen treated with both electrokinetics and water flushing showed OH⁻ advancing further in the initial stages of the experiments. Over a five week remediation programme, the cell only achieved just over 60% overall metal extraction efficiency. Formation of the metal hydroxide precipitates, especially close to the cathode area, was one of the reasons why no near complete removal was experienced. Therefore, designing a model which would check the mobility of OH⁻ species or containing them in a filter or membrane while promoting the migration of the acid front, would be a possible solution in improving the performance of the metal extraction process.

It is implied from conclusions drawn in Section 6.3, that one way of favouring the progression of the acid front further and faster than the base front right from the start of treatment, is by installing a densified ring or barrier of clay (or other suitable material) around the cathode (refer to Figure 6.15). If tested and approved, the ring would be able to hold back the larger OH⁻ ions front while at the same time permitting the passage of the smaller H⁺ ions. Any water trapped in the ring such as that caused by the neutralisation of H⁺ and OH⁻ as well as the electroosmotic water would then be pumped out. Its success would mainly lie in further studies conducted to confirm the specific density requirements for the OH⁻ containment.

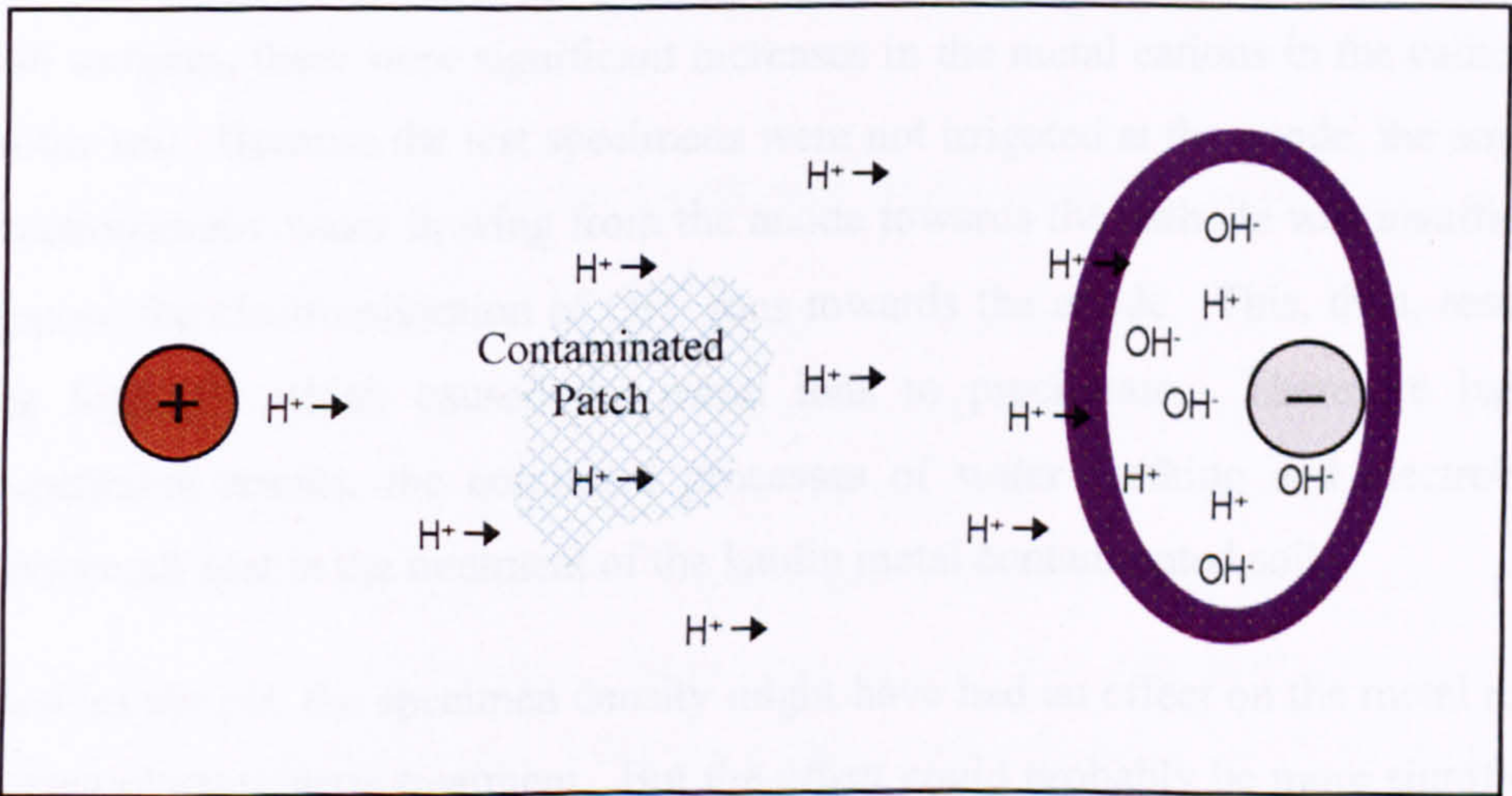


Fig 6.15 Proposed Densified Layer Containing the Hydroxyl Ions at the Cathode

It is anticipated that slowing down the movement of the base front by using the densified barrier proposed in Figure 6.16 would be advantageous in promoting the treatment of the metal contaminated soils. This would be in terms of favouring the migration of the acid front towards the cathode (refer to Section 2.3.2). However, based on the discussion in Section 6.4.1, very stiff/dense clay could also be detrimental in the movement of the metal ions. The barrier stopping the free passage of the 'heavy' OH^- ions would almost certainly prevent the heavier metal cations also, thereby hindering them from filtering into the cathode well where they would be pumped away with the rest of the purge water solution. The solution, however, could be a 'harvesting membrane' which would be denser on the inner side to prevent the passage of the OH^- ions, but porous enough on the outer side to trap the contaminating metal ions – while at the same time allowing the free passage of the H^+ ions. After treatment is over, the membrane would be harvested with the contaminant by pulling it out and taken for disposal.

6.4.6 Interim Conclusions

The metal removal results have shown that:

- 1) During the electrokinetic process, the metal ions concentration generally increased with increase in distance from the anode. The results indicated that the Zn ions were transported from the anode to the cathode during treatment.
- 2) The anode water flushed samples exhibited higher metal removal than the unflushed soil specimens. In both cases, though, there were considerable reductions in concentrations in the anode half of the treated specimens. However, in the unflushed soil samples, there were significant increases in the metal cations in the cathode half of the soil. Because the test specimens were not irrigated at the anode, the amount of electroosmotic water flowing from the anode towards the cathode was insufficient to oppose the electromigration of OH^- ions towards the anode. This, then, resulted in the high pH which caused the metal ions to precipitate. Therefore based on experiment results, the combined processes of water flushing and electrokinetics performed best in the treatment of the kaolin metal contaminated soil.
- 3) Besides the pH, the specimen density might have had an effect on the metal removal during electrokinetic treatment. But the effect could probably be more significant in the cathode region where the clay soil became stiffer and denser as the experiment

duration increased. It is considered that the dense soil inhibited the mobility of the metal ions.

- 4) Test specimens with different heights, but treated under similar conditions, produced identical overall heavy metal extraction efficiencies. The amount of the electrical energy consumed per cubic meter of contaminated soil treated was also nearly the same. Results suggested that electrokinetic treatment was independent of the soil depth if all other parameters were kept constant.
- 5) Samples treated with intermittent currents registered lower metal removal rates especially in the cathode half of the test specimens compared to those which had an uninterrupted current supply. Results showed that in order to achieve the same outcome as the latter, samples with intermittent currents would require more than double the treatment duration.
- 6) In order to optimise the removal efficiency of water flushed electrokinetically treated metal contaminated soils, a 'harvesting membrane' is recommended. This membrane would form a ring around the cathode. The membrane would have to be denser on the inside in order prevent (or slow down) the passage of the OH^- ions, while at the same time permitting the passage of the smaller H^+ ions. But the membrane would be porous enough on the outside perimeter so as to trap the electromigrating metal species into it. Treatment would be completed by pulling out the membrane at the end of the processes and taken for final disposal. Further research into the characteristics of the membrane (such as optimum thickness, density, etc.) as well as its performance with other metal contaminants is recommended.

6.5 Applications and Merits of the Developed EKG Remediation Method

Previous laboratory works on electrokinetic extraction of metals – with diverse approaches, cell models and material characteristics - were aimed at improving the understanding of the fundamental aspect of the process. As noted in the review, the majority of the works were carried out using smaller samples, for far shorter durations and in cells whose all round physical characteristics were not representative of the field conditions. On the other hand, other laboratory methods have not been successfully

applied in the field because of the sophistication of the processing cleansing fluids, with workable electrodes suggested.

Another persistent issue has been the additional treatment enhancements associated to controlling the pH in order to render mobility of the metallic contaminants. Many researchers and practitioners have either proposed, selected or used solubilizing fluids, complexing agents or enhancing solvents (Section 2.3.3.3) to counteract the premature precipitation of metal species close to the cathode compartment. Yet selection of these substances is not only critical but may very often require secondary treatment once the additives have been injected into the soil.

This work also pointed out that some of the full scale electrokinetic methods, like the Lasagna technique, that have been successfully applied in cleaning up sites have been used on limited scale. The time period required for installing the techniques as well as the excavations involved is quite high. Additionally, the cost of hire of specialised machinery is very high as the equipment are not available to local contractors.

It is against this background that the methods used in this study would offer a number of advantages.

In this study, the electrokinetic long term bench scale experiments were carried out in a simple laboratory cell in which no specialised controlling system of, for instance, the anolyte and the catholyte was installed. Techniques of installing the EKG directly and flushing the soil system with deionised water were applied successfully in the laboratory model.

The recommended application for site conditions would involve drilling auger holes and driving the EKG electrodes in the desired grid arrangement of a contaminated fine grained site. Specialised machinery would not be needed as a modified light crane or a simple drilling rig could achieve the desired results. The necessary power could be provided by a DC generator. Using the easily manageable EKG, installed directly in the auger holes, clean water would be poured directly into the anode wells and pumped out directly from the cathode wells. Water, easily abundant and an environmentally friendly natural resource, would adequately serve as the soil flushing and enhancing agent.

Furthermore, for the efficient function of the treatment system, the electrodes used should possess certain qualities. The EKG was capable of dissipating most of the gases produced at the electrodes by diffusing them upwards along the electrode filaments and out. This prevented the disruption of the soil – electrode contact, which would have hampered the process. The EKG system did allow free passage of water from and to the soil. Therefore because of its structure and formation, it ensured that both water and gas got out of the system without any hindrance. Its structure was open to the flow of water and gas yet had sufficient electrical conductivity.

Finally, the laboratory model results of the water flushed soil specimens, successfully showed movement of the metal ions towards the cathode region. By the end of the processing programme, the contaminants had concentrated in a small volume of soil around the cathode electrode. In contrast, the addition of waterlogged-drainage channels aligned along the soil length between the electrodes, and whose water was replenished periodically, produced improved metal removal at the cathode area and lower removals else where. Therefore to achieve much higher extraction efficiency from the former treatment technique, an intermediate drainage channel system should only be installed around the cathode. If however, the ultimate contamination levels at the cathode are still higher than the required threshold, treatment could be completed by digging up the soil material in cathode and taking it for disposal.

CONCLUSIONS AND RECOMMENDATIONS

7.0 Introduction

In this work, the electrokinetic remediation of metal contaminated fine grained soils using EKGs was carried out using saturated Grade E kaolin spiked with Zn ions under uncontrolled conditions. Zn was selected because it is a typically encountered heavy metal contaminant. A comprehensive test programme was established to include two bench scale electrokinetic remediation removal approaches: One Process and Two Process Approaches. The former utilised unenhanced electrokinetic (closed anode) extraction, while the later focussed on the use of electrokinetics in combination with water flushing (open anode) to enhance the effect of electromigration along the soil length. The testing technique enabled the study of effects of: water flushing, soil depth, intermittent currents and replenishing draining chambers along the soil profile with deionised water – on the metal cations removal. Analysis of research results provided important information about the efficiency of the electrokinetic technique for soil treatability as well as the potential of EKGs as electrodes in integrated remediation systems.

This chapter initially summarises the most important conclusions drawn from this research. Then, areas where further efforts motivated by this work would be required are highlighted at the end.

7.1 Summary of Conclusions

The following conclusions are derived from this study:

- 7.1.1 Temporal changes in current during experimentation and its influence on the changes in water flow, water content and contaminant movement and extraction, as well as the effect of current intermittence**

(a) Temporal changes in current during experimentation

1. During the electrokinetic extraction of metals from saturated clay soil samples, using EKGs as electrodes and a constant voltage gradient, the electrical current is highest at the start of the process when the ionic concentration is at its highest. However, due to energy consumption and losses in the test cell, it drops gradually with test duration. The highest drop gradients occur during the initial period of treatment.
2. Once treatment is underway, One Process Approach (with no free access to irrigation water) cells periodically lose current at a much faster rate than Two Process Approach ones (with free access to water). Flushing test soil specimens with water at the anode, as well as operating an intermittent electrical current system (24 hours on / 24 hours off intervals), maintains the electrical power over longer periods.
3. If all test conditions and test material characteristics are maintained, doubling the size of the specimen height causes the measured current to double. Doubling the sample height increases the conductive ions sourced from the soil by twice over resulting into a doubled ionic effect and a doubling of the current.

(b) Influence of current on the changes in water flow and specimen water content

During electrokinetic treatment, current is maximum at the start when the ionic concentration and the average specimen water content are highest. The high electroosmotic flow during the initial period, caused by the high electrical currents, generate large effluent flows from the test specimen. Consequently, the highest reductions in water contents along the length of the test sample occur during this initial period of the treatment. However, as the current gradually falls, the subsequent volume of the effluent water measured from the treated material reduces. Accordingly, the subsequent decreases in the soil material water content lessen.

(c) Effect of current on contaminant movement and extraction

1. Metal cation migration in the soil specimen is highest in the initial period of electrokinetic treatment when the electrical current to the test cell is highest. As the treatment process proceeds and current reduction stabilises, the cation movement rate also reduces.

2. In both One Process and Two Process investigations, the application of a low-voltage current through the soil specimens causes the Zn^{2+} concentration on the anode side of the test cells to drop while effecting a simultaneous increase in metal contamination on the cathode side. This creates a metallic concentration gradient along the test soil length with falling contaminating cations concentration at the anode but rising levels towards the cathode side. This indicates that the stream of metallic cations migrates, under the influence of the applied electric field, in the direction toward the cathode.
3. Due to the continuous application of current, the cathode section and its close proximity becomes the most metal contaminated region of the cell throughout testing. For the One Process treatment, the heavy metal pollutant accumulates highest at a quarter the distance from the cathode while under the Two Process conditions, it concentrates at the cathode.
4. The accumulation of the metal before the cathode especially in the One Process treatment, mainly due to Zn^{2+} coming out of solution, impedes the extraction of the contaminating cation from the soil specimen.
5. Conducting current intermittence intervals of 24 hours on and 24 hours off during cleaning up, achieves identical metal removal rates in the anode half and lower removals in the cathode half of the test specimens compared to those with uninterrupted direct current supply. In order to register the same overall removal efficiency as the latter, samples with intermittent currents would require longer treatment duration.

7.1.2 Relationship with time of the amount of the Zn^{2+} extracted along both the length and vertical depth of the cell with and without flushing of deionised water

- 1) When the electrokinetic treatment starts, Zn^{2+} begins to electromigrate towards the cathode. The process causes the metal cations to progressively be transported in the direction anode to the cathode. Therefore the contaminant concentration in the specimen generally increases with increase in the cell length towards the cathode.
- 2) In the One Process and Two Process treatments, the highest removal of the metal ions along the length of cell is achieved in the initial period. In this study it was the first

two weeks of treatment. By this period alone, the metal concentration in the anode half of the cell of the One Process and Two Process conditions tests had respectively dropped by 65 and 80%.

- 3) All positions along the length of the test cells, (with the exception of those of the One Process Approach) experience decline in average cell metal concentrations with time.
- 4) Generally, the periodic metal extraction in all the three layers; top, middle and bottom were not significantly different. The top and bottom do not appear to be appreciably affected by the boundary effects.
- 5) Bench scale specimens with different heights, but treated under similar conditions, produce identical overall heavy metal extraction efficiencies. The amount of the electrical energy consumed per cubic meter of contaminated soil treated is also comparable. Doubling the height of the soil to be treated, while maintaining similar process conditions, does not appear to affect the overall metal migration characteristics during the joint application of electrokinetic and soil flushing processes.

7.1.3 Effect of the spatial changes in water content on the effectiveness of contaminant removal.

1. Electrokinetic process induces water to flow in the direction of the cathode. However, this uni-directional movement of pore water, followed by the insufficient supply of the pore fluid from the anode, due to the low permeability of the clay soil, causes suction to develop across the specimen. This then causes the soil to reduce in volume. This development along with other physicochemical changes results in the gradual reduction of the electroosmotic permeability consequently reducing the electroosmotic flow. This affects the electrokinetic process accordingly.
2. The moisture within the soil mass generally decreases with time during the electrokinetic process of both One Process and Two Process conditions. The highest drop in soil water content occurs during the initial stages of cleaning (1 week in this study), with subsequent periodic decreases in water content values falling with increase in test duration.

For the irrigated anode conditions, however, the decreases in pore water are minimal beyond the first stage (second week in this study) of treatment as residual water content values are being established within the cell.

3. Most metal extraction is achieved in the initial stages of the electrokinetic treatment when the water content is highest. Metal cation mobility is enhanced when the metal is in the dissolved state and the water content is sufficiently high.
4. The unflushed soil samples lose more water with time during electrokinetic treatment. While samples supplied with water constantly to the anode electrodes, during treatment, maintain higher spatial water contents right through the specimen. The higher water content in the latter implied that the zinc metal remained in solution relatively longer resulting in better contaminant removal rates. In the One Process, however, the periodically falling cell water content impeded the movement of the zinc resulting in lower metal cation removal.
5. The spatial and temporal changes of water content in soil specimens with the same horizontal length and test conditions, but different heights were nearly the same although slight changes were evident. These slight changes could be attributed to minor variations in the electroosmotic flow and probably some procedural errors. This implies that height may not seem to significantly affect the electrokinetic migration characteristics.

7.1.4 Determine whether maintaining a stream of clean water in channels directly installed in the contaminated soil enhanced metal removal.

1. At any specific time during the clean up operation, the highest spatial water contents are generally experienced by the specimens with replenished drainage channels. Having waterlogged drainage channels along the soil profile increases the water available in the soil specimens during electrokinetic treatment.
2. Addition of waterlogged-drainage channels aligned along the soil length between the electrodes, and whose water is replenished periodically, improves the metal removal at the cathode area. Elsewhere in the cell, however, lower metal removals than specimens tested without the replenished drainage chambers are realized.

7.1.5 Evaluate the temporal and spatial variation in pH during electroosmosis and its influence on contaminant removal.

1. During the electrokinetic treatment, a distinct pH gradient is created in the kaolin soil specimen ranging from 2.3 at the anode to 10.6 near the cathode. This is due to the electrolysis reactions at the anode and cathode electrodes. The production of H^+ ions at the anode decreases the pH, while production of OH^- ions at the cathode increases the pH ions.
2. Based on the Two Process research test conditions, it is considered that the pH movement is in two major phases. The first phase occurs in the opening stages of treatment when the test specimen is saturated and less dense. At that time the base front advances towards the anode faster than the acid front. The second phase occurs later on when the advancement of the acidic front in the opposite direction is faster. At latter stage, the water content is lower than that at the start. The reduction in soil specimen water content is steadier and the sample is fairly stiff and denser especially at the cathode area.
3. In both One Process and Two Process treatment, there were considerable reductions in Zn^{2+} concentrations in the anode half of the treated specimens. However, in the unflushed soil samples, there were significant increases in the metal cations in the cathode half of the soil caused by high pH. Because the test specimens were not irrigated at the anode, the amount of electroosmotic water flowing from the anode towards the cathode was insufficient to oppose the electromigration of OH^- ions towards the anode. This, then, resulted in the high pH which caused the Zn^{2+} ions to precipitate thereby hindering the metal removal.

7.2 Removal Efficiency

Generally the removal efficiencies obtained in this study were lower than those from the reviewed literature. The efficiencies ranged between 15% (for specimens under only electrokinetic decontamination) to nearly 64% (for those under combined treatment of electrokinetic and soil washing technologies). It was observed, however, the energy required to decontaminate a cubic meter of soil ranged between 4 and 14KWh. This was much lower than those reported in literature (between 25 and 700KWh). The influence

of the variations: e.g. type of electrodes, open or closed anode conditions, size of tank, use of Zn rather than Pb, Cd, Cr, Cu etc., use of slurry soil, difference in starting concentrations relative to CEC, etc. was the explanation to these difference.

7.3 Recommendations

The following are the studies recommendations for future study:

- 1) The efficiency of the electrokinetic process for heavy metal removal depends on the extent to which the acid front reaches the cathode. Therefore, in order to favour the progression of H^+ ions front further and faster than the OH^- ions front, then a densified ring or barrier around the cathode is recommended. However, further study to determine its characteristics (such as thickness, density, etc.) as well as its performance with other metal contaminants needs to be further investigated.
- 2) In order to optimise the removal efficiency of water flushed electrokinetically treated metal contaminated soils, a harvesting membrane is recommended. This membrane would form a ring around the cathode. The membrane would have to be denser on the inside in order prevent (or slow down) the passage of the OH^- ions, but porous enough on the outside perimeter so as to trap the electro migrating metal species into it. Treatment would be completed by pulling out the membrane at the end of the processes and taken for final disposal. Further research into the characteristics of the membrane is recommended.
- 3) An algorithm has also been developed for back prediction of the current requirements for the cells used in this study. However further development of this equation through further studies so that if the polluted soil material, contaminant characteristics and test conditions are known, then the equation constant characteristics could be established straight away. Also, if well developed, the equation would make it possible to make power estimates from a single laboratory test.
- 4) The development of cracks - at the soil top surface as well as between the electrodes and soil - as the test progressed was a major problem encountered. In this study, the cracks were repaired as soon as they became visible by using a wooden block and gently pressing the top soil in the same vicinity until they closed. Large current losses were observed with the development of cracks especially overnight when the tests

were left unattended to for long (about 12 hours). Although, the crack repairing minimised the inefficiencies, a mechanism that could take control within itself would be more appropriate. This would ensure that more electrical energies are translated into higher decontamination efficiency. Further study into this system is recommended.

- 5) Although this work recommends full-scale site application of this technology for remediation of heavy metals contaminated fine soils, the technology could itself be limited at best, until field investigations are conducted so as to resolve these additional issues and concerns:
- (a) The bench scale treatability tests, as they were designed in this study, could not identify the potential for by-product production. Yet, presence of naturally occurring ions and organic material as well as organic contaminants (in the field conditions) could result in the development of potentially hazardous by-products (such as chlorine, trihalomethanes, acetone, etc.) when an electric field is applied to the soil.
 - (b) The retarding effects created by the naturally occurring ions can not be accurately quantified in the laboratory tests and their effects on the type of metal species formed under the electric field influence cannot be accurately predicted. A study which provides an understanding of the technology's effects on naturally occurring ions and how these effects impact mobilization and removal of the target contaminants is essential.
 - (c) The impact that electrokinetic extraction had on the physical and chemical characteristics of the soil was not addressed at all in this research as it was not in its objectives. Yet these characteristics could individually or cumulatively have impacted the extraction rate and efficiency of the technology. Therefore, the changes to the soil (including the potential ecological impacts) after cleanup target levels have been reached need to be thoroughly investigated.

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Appendix

Computations

A.1 Zinc Concentration in the Test Sample

The concentration of contaminated soil was 680 mg of dry zinc chloride (ZnCl_2) crystals per 8 kg of dry kaolin

Atomic mass of Zn is 65.38 g.mol^{-1}

Atomic mass of Cl is 35.45 g.mol^{-1}

$$\begin{aligned} \text{Amount of Zn}^{2+} \text{ in 680 mg of ZnCl}_2 &= \frac{65.38}{(65.38 + [2 \times 35.45])} \times 680 \\ &= 326.23 \text{ mg} \end{aligned}$$

This is equivalent to a Zn^{2+} concentration of 326.23 mg per 8 kg of kaolin

$$\begin{aligned} \text{Zn}^{2+} \text{ available per kg of kaolin} &= \frac{326.23}{8} \\ &= 40.8 \text{ mg/kg of kaoline} \end{aligned}$$

$$\text{Or} \quad = 4.08 \text{ g / 100g of kaoline}$$

Cation exchange capacity of Kaolin (CEC) = 3 meq / 100 g of dry kaolin soil mass (refer to *Section 2.3.2*)

$$1 \text{ equivalent} = 1 \text{ mole of unit charge} = 0.5 \text{ moles of Zn}^{2+}$$

$$\therefore 1 \text{ meq} = 0.5 \text{ mmol of Zn}^{2+}$$

Assuming the CEC of Kaolin is equivalent to the exchange capacity status (ECS) of Zn^{2+} when mixed with kaolin (i.e. all cation exchangeable sites are taken up by Zn^{2+});

$$\text{Then} \quad \text{ECS}_{(\text{Zn}^{2+})} = 3 \text{ meq / 100 g}$$

$$\text{But} \quad 1 \text{ mol of Zn}^{2+} = 65.38 \text{ g}$$

$$\begin{aligned} \therefore 3 \text{ meq of Zn}^{2+} &= 3 \times 0.5 \times 65.38 \\ &= 98.07 \text{ mg} \end{aligned}$$

∴ Amount of Zn^{2+} that would freely bind with kaolin is 98 mg / 100 g of dry soil

The percentage of Zn^{2+} in contaminated soil at the start was about,

$$= \frac{4.08}{98} \times 100$$

$$= 4.2\% \text{ of the CEC of the kaolin}$$

A.2 Statistics Equations Used

$$1. \quad \text{Average} = \frac{\sum \text{Score}}{N}$$

where N is the number of Scores

$$2. \quad \text{Deviation} = \text{Score} - \text{Average}$$

$$3. \quad \text{Standard Deviation} = \sqrt{\left[\frac{\sum (\text{Deviations})^2}{N-1} \right]}$$

Figures

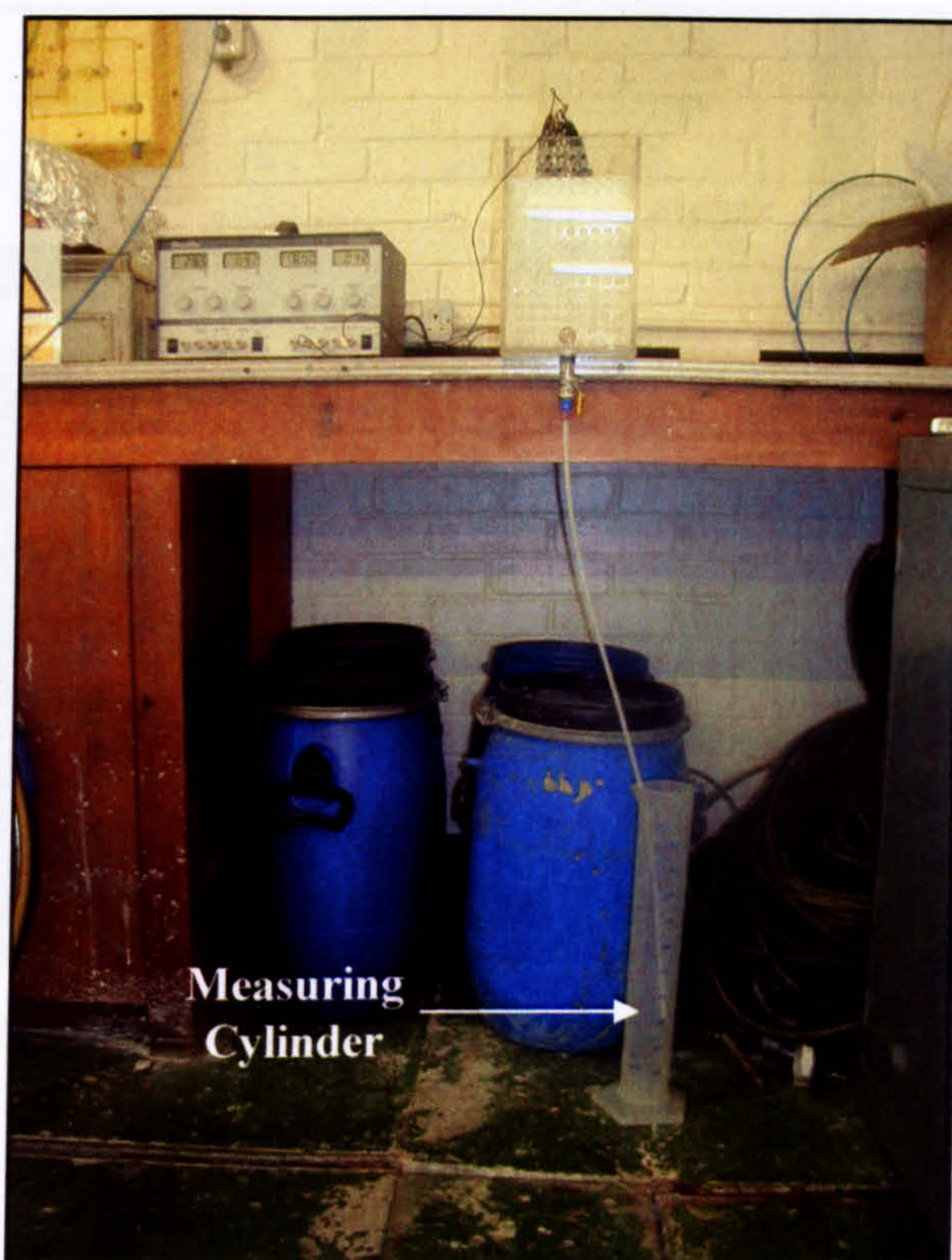


Fig A4.1 Plastic Tubing from Effluent Chamber Leading into Measuring Cylinder



Fig A4.2 Ultrameter Model 6P used for Determining pH

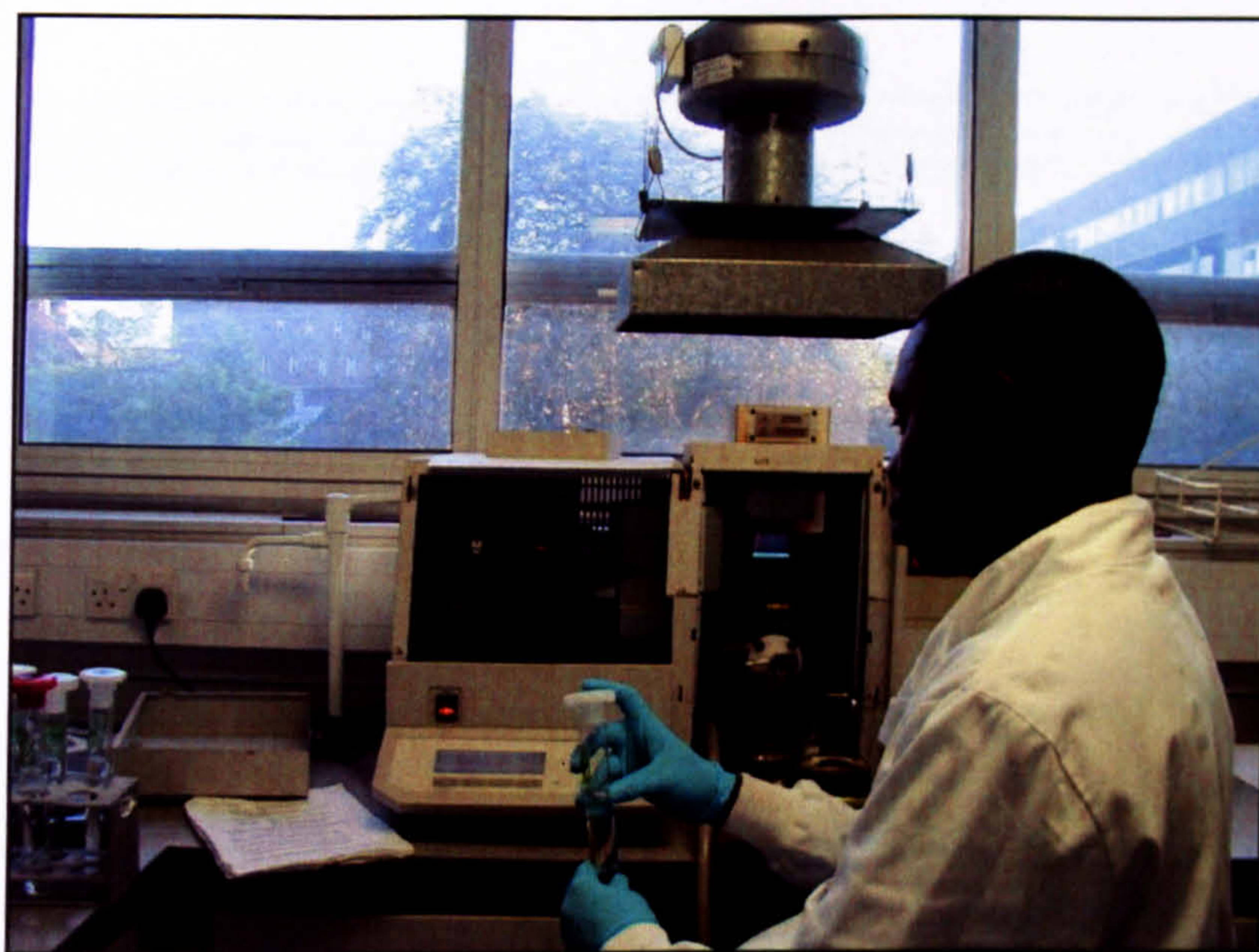


Fig A4.3 Determination of Zinc Ions Using the UNICAM 929 Atomic Absorption Spectrometer

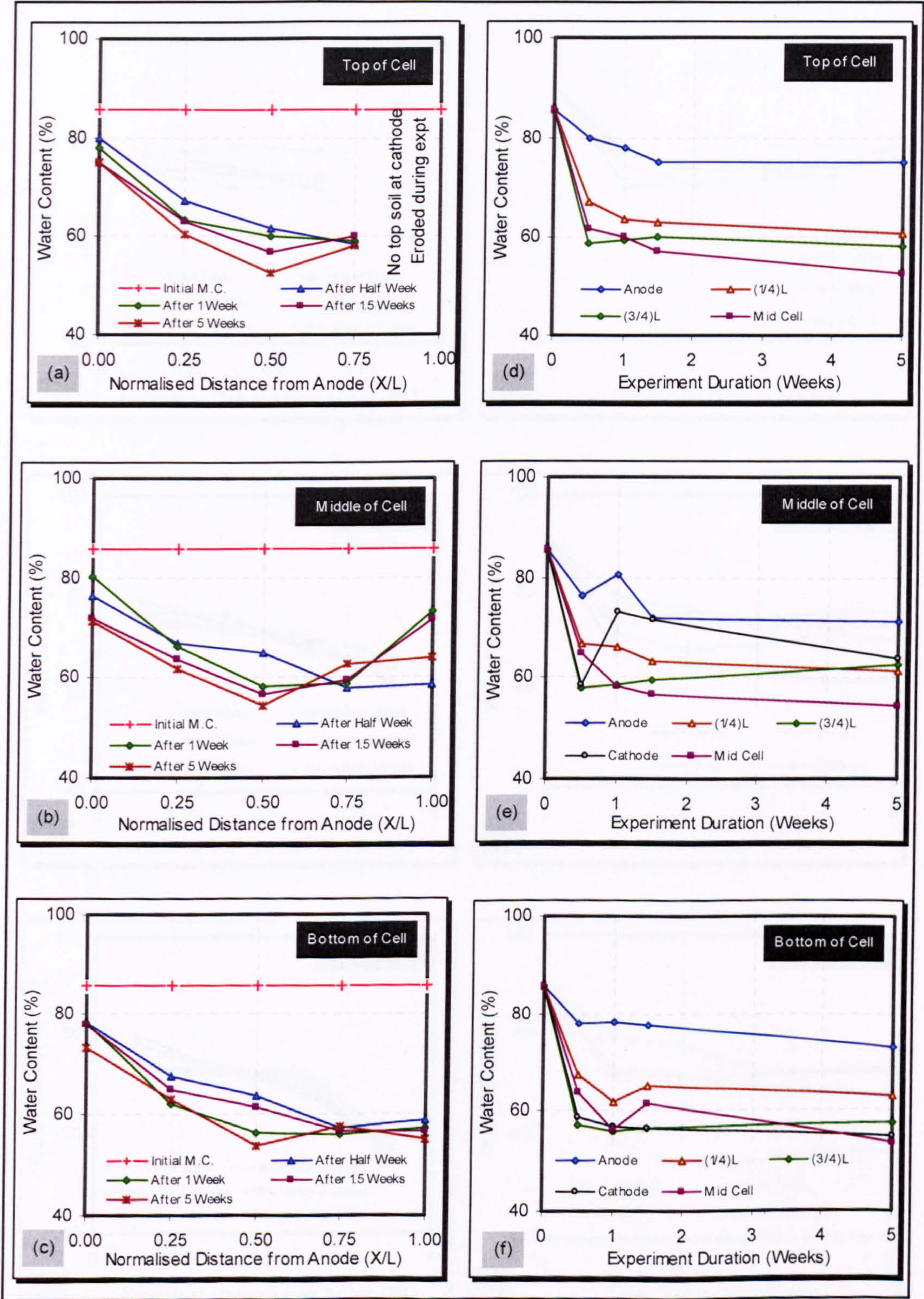


Fig A5.1 Variation of WC: along cell (a, b, c) and with Time (d, e, f) - Flushing at the Anode with Intermittent Currents ($H = 150\text{mm}$)

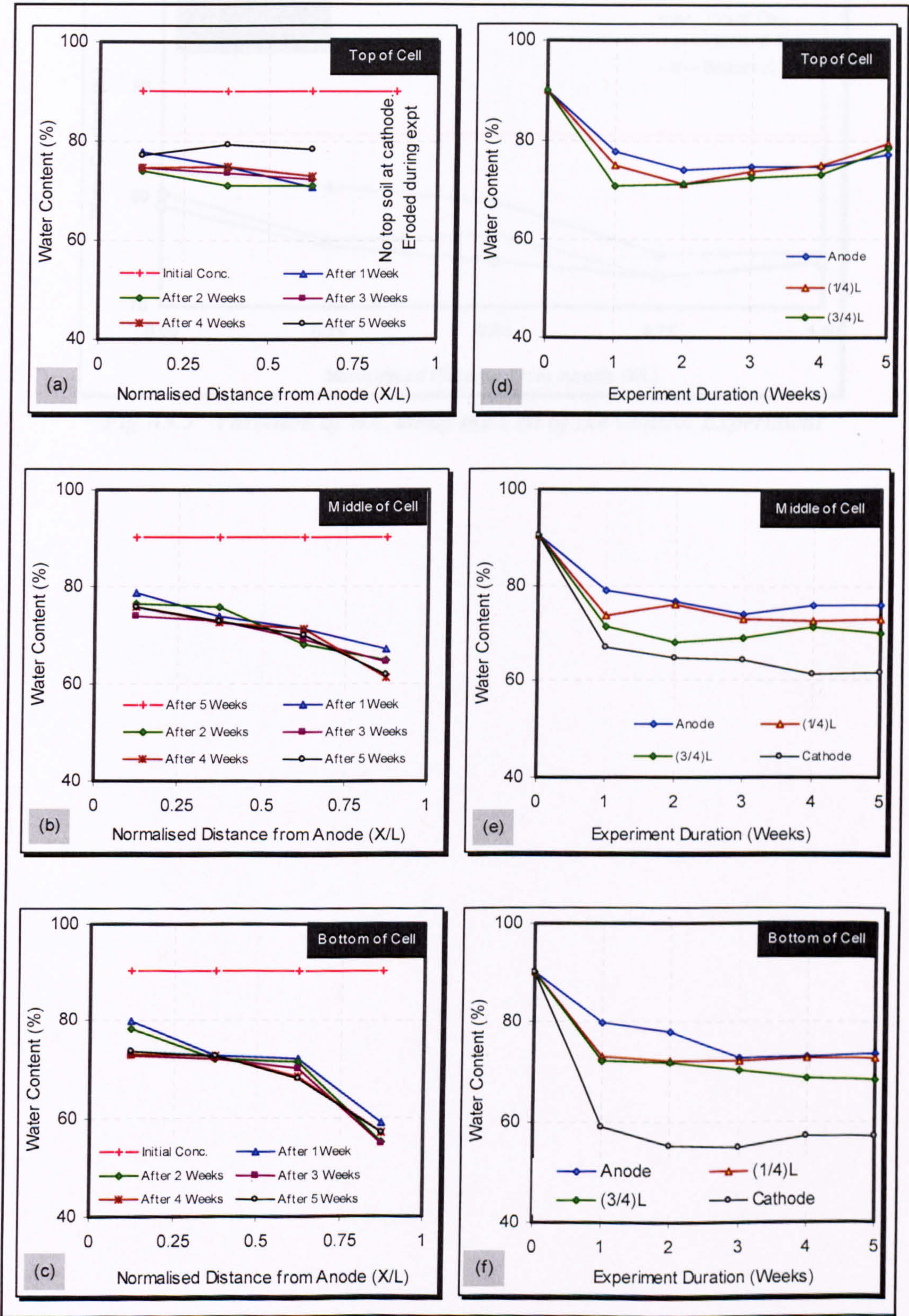


Fig A5.2 Variation of WC: along cell (a, b, c) and with Time (d, e, f) - with Replenished Drainage Channels

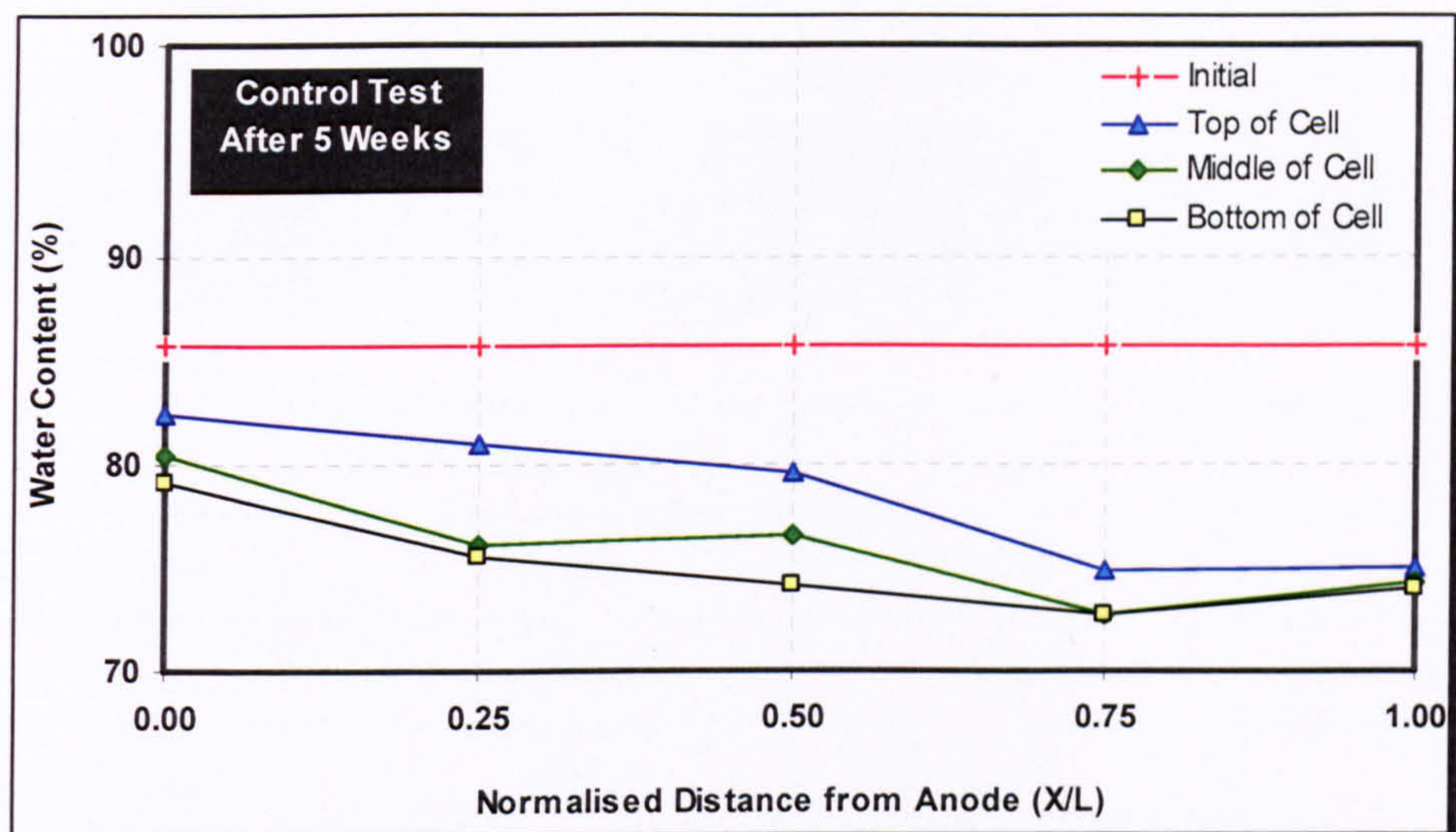


Fig A5.3 Variation of WC along the Cell of the Control Experiment

Table A5.1. Monthly Average Changes in Current and Total Inventories

	1982	1983	1984	1985
1. Current	0.00	0.00	0.00	0.00
2. Total	0.00	0.00	0.00	0.00
3. Current	0.00	0.00	0.00	0.00
4. Total	0.00	0.00	0.00	0.00
5. Current	0.00	0.00	0.00	0.00
6. Total	0.00	0.00	0.00	0.00

Table A5.2. Monthly Average Changes in Inventories with 24-hour or more delay

	1982	1983	1984	1985
1. Current	0.00	0.00	0.00	0.00
2. Total	0.00	0.00	0.00	0.00
3. Current	0.00	0.00	0.00	0.00
4. Total	0.00	0.00	0.00	0.00
5. Current	0.00	0.00	0.00	0.00
6. Total	0.00	0.00	0.00	0.00

Table

Table A5.1 Weekly Average Changes in Current without Flushing at Anode

Period from Start of Experiment	Average Weekly Current (A)	Change in Current Per Week (A)	Percentage Changes
Beginning	0.048	-	-
1 Week	0.007	0.041	85.4
2 Weeks	0.003	0.004	8.3
3 Weeks	0.002	0.001	2.1
4 Weeks	0.001	0.001	2.1
5 Weeks	0.000	0.001	2.1

Table A5.2 Weekly Average Changes in Current with Flushing at Anode for H = 150mm

Period from Start of Experiment	Average Weekly Current (A)	Change in Current Per Week (A)	Percentage Changes
Beginning	0.048	-	-
1 Week	0.0123	0.0361	74.6
2 Weeks	0.009	0.0033	6.8
3 Weeks	0.0063	0.0027	5.5
4 Weeks	0.0055	0.0008	1.7
5 Weeks	0.005	0.0005	1.0

Table A5.3 Volume of Effluent Measured from the Control Experiment over the 5 Weeks Treatment Period

Duration (Weeks)	Measured Volume Effluent (ml)	Cumulative Volume of Effluent (l)
0	0	0.010
0.202	50	0.050
0.315	42.5	0.093
0.429	35	0.128
0.571	36	0.164
0.857	55	0.219
1	20.5	0.239
1.429	64.5	0.304
1.714	37	0.341
2	37	0.378
2.429	56	0.434
2.714	31	0.465
3	28	0.493
3.429	48	0.541
3.714	29	0.570
4	19	0.589
4.429	44	0.633
4.756	32	0.665
5	28	0.693

Table A5.4 Zinc Concentration and Quantity of Effluent Water and Suspended Solids in Effluent from the One Process Experiment over the 5 Weeks Treatment Period

Duration (weeks)	Volume of Water (H ₂ O) in Effluent (ml)	Cumulative Volume of Water (l)	Mass of Solids in Effluent (g)	Cumulative Mass of Solids (kg)	Total Effluent, (H ₂ O + Solids) (g)	Total Cumulative Effluent (kg)	Measur- ed Zn Conc. in Effluent H ₂ O (mg/l)	Total Zn in Effluent H ₂ O (mg)	Cumulative Zn in Effluent H ₂ O (mg)	Measu- red Zn Conc. in Solids (mg/kg)	Total Zn in Solids (mg)	Cumulative Zn in Effluent Solids (mg)	Total Cumulative Zn in H ₂ O + Solids (mg)
0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.000	0.000	0.000	0.000	0.000	0	0
0.143	966.83	0.967	118.17	0.118	1085	1.09	0.264	0.256	0.256	81.08	9.582	9.58	9.84
0.286	780.00	1.747	63.250	0.181	760	1.85	0.391	0.273	0.528	84.67	5.355	14.94	15.47
0.429	321.13	2.068	13.870	0.195	335	2.18	0.405	0.130	0.658	120.42	1.670	16.61	17.27
0.571	150.90	2.219	5.551	0.201	156.45	2.34	0.243	0.0367	0.695	125.91	0.699	17.31	18.00
1.000	94.45	2.313	3.151	0.204	97.60	2.43	0.003	0.0003	0.695	80.92	0.255	17.56	18.26
1.500	0.000	2.313	0.000	0.204	0.00	2.43	0.000	0.000	0.695	0.000	0.000	17.56	18.26
2.000	0.000	2.313	0.000	0.204	0.00	2.43	0.000	0.000	0.695	0.000	0.000	17.56	18.26
3.000	0.000	2.313	0.000	0.204	0.00	2.43	0.000	0.000	0.695	0.000	0.000	17.56	18.26
4.000	0.000	2.313	0.000	0.204	0.00	2.43	0.000	0.000	0.695	0.000	0.000	17.56	18.26
5.000	0.000	2.313	0.000	0.204	0.00	2.43	0.000	0.000	0.695	0.000	0.000	17.56	18.26

Table A5.5 Zinc Concentration and Quantity of Effluent Water and Suspended Solids in Effluent from the Two Process Experiment over the 5 Weeks Treatment Period

Duration (weeks)	Volume of Water (H ₂ O) in Effluent (ml)	Cumulative Volume of Water (l)	Mass of Solids in Effluent (g)	Cumulative Mass of Solids (kg)	Total Effluent, (H ₂ O + Solids) (g)	Total Cumulative Effluent (kg)	Measur- ed Zn Conc. in Effluent H ₂ O (mg/l)	Total Zn in Effluent H ₂ O (mg)	Cumulative Zn in Effluent H ₂ O (mg)	Measur- ed Zn Conc. in Solids (mg/kg)	Total Zn in Solids (mg)	Cumulative Zn in Effluent Solids (mg)	Total Cumulative Zn in H ₂ O + Solids (mg)
0.000	0.00	0.000	0.000	0.000	0.00	0.00	0.000	0.000	0.000	0	0.000	0	0.00
0.143	1180.71	1.181	129.29	0.129	1310.00	1.31	0.152	0.179	0.179	81.303	10.512	10.51	10.69
0.286	908.85	2.090	76.150	0.205	985.00	2.30	0.158	0.144	0.323	106.26	8.092	18.60	18.93
0.449	597.23	2.687	42.770	0.248	640.00	2.94	0.660	0.394	0.717	122.84	5.254	23.86	24.58
0.622	440.43	3.127	14.570	0.263	455.00	3.39	0.095	0.042	0.759	115.72	1.686	25.54	26.30
0.760	276.15	3.403	8.850	0.272	285.00	3.68	0.097	0.027	0.786	122.11	1.081	26.62	27.41
0.893	233.97	3.637	6.030	0.278	240.00	3.92	0.066	0.015	0.801	108.10	0.652	27.28	28.08
1.033	231.63	3.869	3.373	0.281	235.00	4.15	0.056	0.013	0.814	117.52	0.396	27.67	28.49
1.615	539.88	4.409	0.120	0.281	540.00	4.69	0.050	0.027	0.841	162.41	0.019	27.69	28.53
2.000	184.89	4.594	0.105	0.281	185.00	4.88	0.041	0.008	0.849	115.22	0.012	27.70	28.55
2.429	154.91	4.749	0.092	0.281	155.00	5.03	0.026	0.004	0.853	99.54	0.009	27.71	28.57
3.000	149.97	4.899	0.033	0.281	150.00	5.18	0.021	0.003	0.856		0.000	27.71	28.57
4.000	150.00	5.049	0.000	0.281	150.00	5.33	0.018	0.003	0.859		0.000	27.71	28.57
5.000	135.00	5.184	0.000	0.281	135.00	5.47	0.011	0.001	0.860		0.000	27.71	28.57

Table A5.6 Weight and Zinc Concentration Ratios for the Periodically Collected Effluent Water and Suspended Solids of the Two Electrokinetic Tests

Two Process Approach			One Process Approach		
Test Duration (weeks)	$\frac{\text{Mass of Solids}}{\text{Mass of Water}}$	$\frac{\text{Zn Conc. in Solids}}{\text{Zn Conc. in Water}}$	Test Duration (weeks)	$\frac{\text{Mass of Solids}}{\text{Mass of Water}}$	$\frac{\text{Zn Conc. in Solids}}{\text{Zn Conc. in Water}}$
0.000	-	-	0.000	-	-
0.143	0.110	721.09	0.143	0.010	306.75
0.286	0.084	528.99	0.286	0.008	216.32
0.449	0.072	108.52	0.429	0.005	297.59
0.622	0.033	349.47	0.571	0.005	518.16
0.760	0.032	332.06	1.000	0.003	26974.30
0.893	0.026	393.46			
1.033	0.015	258.58			
1.615	0.000	4.44			
2.000	0.001	13.88			
2.429	0.001	22.44			
3.000	0.000	10.12			
4.000	0.000	0.00			
5.000	0.000	0.00			

Table A5.7 Zn Mass Distribution along Specimen Length After 5 Weeks for the One Process Experiment

Normalised Distance from Anode	Zn Concentration (mg/kg)			Water Content Determination					Soil Specimen Mass (kg)			Zn Mass (mg)		
	Top	Middle	Bottom	Tin (g)	Tin + Wet Soil (g)	Tin + Dry Soil (g)	Dry Soil (g)	WC (%)	Top	Middle	Bottom	Top	Middle	Bottom
0.00	16.94	11.15	21.06	644.10	1968	1632.8	988.7	33.9	0.330	0.330	0.330	5.583	3.675	6.941
0.25	10.05	12.64	7.41	460.87	2589.2	2046.8	1585.93	34.2	0.529	0.529	0.529	5.313	6.682	3.917
0.50	18.59	23.31	18.47	646.80	2712.1	2188.4	1541.6	34.0	0.514	0.514	0.514	9.553	11.978	9.491
0.75	141.43	173.44	66.33	638.7	2511.5	2031.4	1392.7	34.5	0.464	0.464	0.464	65.654	80.517	30.793
1.00	0	62.99	38.06	156.66	1140.68	891.81	735.15	33.9	0.245	0.245	0.245	0.000	15.436	9.327
Sub total of Zn Mass														
Total Mass of Zn in Cell at End of Treatment														
												86.103	118.287	60.468
264.858														

Table A5.8 Zn Mass Distribution along Specimen Length After 5 Weeks for the Two Process Experiment

Normalised Distance from Anode	Zn Concentration (mg/kg)			Water Content Determination					Soil Specimen Mass (kg)			Zn Mass (mg)		
	Top	Middle	Bottom	Tin (g)	Tin + Wet Soil (g)	Tin + Dry Soil (g)	Dry Soil (g)	WC (%)	Top	Middle	Bottom	Top	Middle	Bottom
0.00	74.59	10.83	109.47	1127.90	3324.10	2453.30	1325.40	65.70	0.442	0.442	0.442	32.953	4.785	48.363
0.25	10.25	8.68	8.20	644.00	2760.70	2055.50	1411.50	49.96	0.471	0.471	0.471	4.822	4.084	3.859
0.50	9.12	10.52	9.19	638.60	3308.00	2456.10	1817.50	46.87	0.606	0.606	0.606	5.523	6.375	5.567
0.75	7.97	9.98	9.69	646.70	2606.90	1934.70	1288.00	52.19	0.429	0.429	0.429	3.423	4.286	4.161
1.00	0.00	62.53	44.77	460.78	1972.30	1453.50	992.72	52.26		0.496	0.496	0.000	31.036	22.221
Sub total of Zn Mass												46.720	50.566	84.172
Total Mass of Zn in Cell at End of Treatment												181.459		

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